A TEXT-BOOK OF
INORGANIC CHEMISTRY.
VOLUME III. PART I.

Series	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
First short period	2 He 4·00	1 H 1·008							
Second short period	10 Ne 20·2	3 Li 6·940	4 Be 9·02	5 B 10·82	6 C 12·000	7 N 14·008	8 O 16·000	9 F 19·00	
First long period — Even series	18 A 39·91	19 K 39·096	20 Ca 40·07	21 Sc 45·10	22 Ti 48·1	23 V 50·96	24 Cr 52·01	25 Mn 54·93	26 Fe 55·84, 27 Co 58·94, 28 Ni 58·69
First long period — Odd	36 Kr 82·9	29 Cu 63·57	30 Zn 65·38	31 Ga 69·72	32 Ge 72·60	33 As 74·96	34 Se 79·2	35 Br 79·916	
Second long period — Even series		37 Rb 85·44	38 Sr 87·63	39 Y 88·9	40 Zr 91·0	41 Cb 93·1	42 Mo 96·0	43	44 Ru 101·7, 45 Rh 102·91, 46 Pd 106·7
Second long period — Odd	54 X 130·2	47 Ag 107·880	48 Cd 112·41	49 In 114·8	50 Sn 118·70	51 Sb 121·77	52 Te 127·5	53 I 126·932	
Third long period		55 Cs 132·81	56 Ba 137·37	57 La 138·90	58 Ce 140·25 / 59 Pr 140·92	60 Nd 144·27 / 61	62 Sm 150·43 / 63 Eu 152·0	64 Gd 157·26 / 65 Tb 159·2	
Third long period (rare earths)		66 Dy 162·52 / 67 Ho 163·4	68 Er 167·7 / 69 Tm 169·4	70 Yb 173·6 / 71 Lu 175·0 [180·8]					
Fourth long period					72 Ct [180·8]	73 Ta 181·5	74 W 184·0	75	76 Os 190·8, 77 Ir 193·1, 78 Pt 195·23
Fifth long period — Even series	86 Rn 222	79 Au 197·2	80 Hg 200·61	81 Tl 204·39	82 Pb 207·20	83 Bi 209·00	84 Po [210]	85	
Fifth long period — Odd		87	88 Ra 225·95	89 Ac	90 Th 232·15	91 Pa	92 U 238·17		
Volume in this series of text-books.	1	2	3	4	5	6	7	8	9

* The International Atomic Weights for 1925 are adopted in this Table

A TEXT-BOOK OF

INORGANIC CHEMISTRY.

EDITED BY

J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,

CARNEGIE GOLD MEDALLIST

VOLUME III. PART I.

THE ALKALINE EARTH METALS.

BY

MAY SYBIL BURR (NÉE LESLIE),

D Sc (LEEDS)

With Frontispiece and Illustrations.

GENERAL INTRODUCTION TO THE SERIES

DURING the past few years the civilized world has begun to realize the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches : namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned ; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the elements of Group 0, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasize their application to Inorganic Chemistry, with which the subject this series of text-books is exclusively

PREFACE

THE elements described in this volume claim u.
for very varied reasons. In the first place they
mercury, which excited the wonder and curiosity of ι.
another, radium, which has equally excited the wonder .
of the moderns. A group of historical interest is formed by m.
calcium, strontium, and barium, upon the oxides of which,
more than a century ago, Davy was able to show the decompos.
action of the electric current. Beryllium is famous historically for the
long controversy as to its position in the Periodic Table. Zinc has
been known since very early times, chiefly through its association
with copper to form brass, but also as sulphate, the " white vitriol "
of the alchemists. Cadmium, although similar to zinc in many of its
properties, has only been recognised since the beginning of the last
century.

Part I of Volume III is devoted to the study of the four alkaline
earths alone. As regards chemical properties, they form a very closely
related series of elements, so closely related, indeed, that the properties
of one element might often be calculated with a fair degree of exactitude
consideration of the properties of the others.
properties, on the other hand, one element, radium,
possessor of extraordinary characteristics of which
any of the other three. The recognition of the
similar bodies, of a continuous supply of
visible manifestation is the luminescence
at and its salts, if present in sufficient
change which must be classed as a
has revolutionised modern views
the last quarter of a century.
indicated to the analyst as a
been known, for the detec-
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would such
, out summaries
.e understanding of
.ous references accom-
.urther details to obtain
.ory account of radium apart
.ives. A little overlapping with
.nerefore, on that account, unavoid-
.adium, since the physical rather than
.ie element have been the favourite object
.iy display features not common to the other

.ias been made to render the references as complete
.o possible. Atomic weights have been recalculated from
. experimental data on the basis employed throughout the
.id indicated in the General Preface.

.ne Author offers her sincere thanks to the General Editor, Dr. J.
.iewton Friend, who has read the whole of the manuscript and proof,
for the courteous interest he has taken in the progress of the work, and
for the helpful counsel he has always been willing to place at her disposal.
She is also indebted to her husband, Mr. A. H. Burr, for much valuable
assistance in proof-correcting and indexing.

<div align="center">MAY SYBIL BURR (née LESLIE).</div>

CONTENTS.

LIST OF CHIEF ABBREVIATIONS EMPLOYED
IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
Afhandl. Fys. Kem.	Afhandlingat i Fysik, Kemi och Mineralogi.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815 and 1914 +).
Ann. Chim. anal	Annales de Chimie analytique appliquée à l'Industrie, a l'Agricultura, à la Pharmacie, et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique (Paris) (1816–1913).
Ann. Mines	Annales des Mines.
Ann. Pharm.	Annalen der Pharmacie (1832–1839).
Ann. Phys. Chem.	Annalen der Physik und Chemie (1819–1899).
Ann. Physik	Annalen der Physik (1799–1818, and 1900 +).
Ann. Physik, Beibl.	Annalen der Physik, Beiblatter.
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arbeiten Kaiserl. Gesundheitsamte	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
Arch. exp. Pathol. Pharmak.	Archiv fur experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles, Genève.
Atti Acc. Torinò	Atti della Reale Accademia delle Scienze di Torinò.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
B A. Reports	British Association Reports.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bot. Zeit.	Botanische Zeitung.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. de Belg.	Bulletin de la Société chimique Belgique.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. min. de France	Bulletin de la Société minéralogique de France.
Bull. U.S. Geol. Survey	Bulletins of the United States Geological Survey.
Centr. Min.	Centralblatt fur Mineralogie.
Chem. Ind.	Die Chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad.	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Crell's Annalen	Chemische Annalen fur die Freunde der Naturlehre, von L. Crelle.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Drude's Annalen	Annalen der Physik (1900–1906).
Electrochem. Met. Ind.	Electrochemical and Metallurgical Industry.

Abbreviated Title.	Journal.
Eng. and Min. J.	Engineering and Mining Journal.
Gazzetta	Gazzetta chimica italiana.
Gehlen's Allg. J. Chem.	Allgemeines Journal der Chemie.
Gilbert's Annalen	Annalen der Physik (1799–1824).
Giorn. di Scienze Naturali ed Econ.	Giornale di Scienze Naturali ed Economiche.
Geol. Mag.	Geological Magazine.
Int. Zeitsch. Metallographie	Internationale Zeitschrift fur Metallographie.
Jahrb kk. geol. Reichsanst.	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
Jahrb. Miner.	Jahrbuch fur Mineralogie.
Jahresber.	Jahresbericht uber die Fortschritte der Chemie.
Jenaische Zeitsch.	Jenaische Zeitschrift tur Naturwissenschaft.
J. Amer. Chem. Soc	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim phys.	Journal de Chimie physique.
J. Gasbeleuchtung	Journal fur Gasbeleuchtung.
J. Geology	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Metals	Journal of the Institute of Metals.
J. Miner. Soc.	Mineralogical Magazine and Journal of the Mineralogical Society.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physique	Journal de Physique.
J. prakt. Chem.	Journal fur praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (Petrograd)
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb	Landwirtschaftliche Jahrbucher.
Mém. Paris Acad.	Mémoires présentés par divers savants à l'Académie des Sciences de l'Institut de France.
Mon. scient.	Moniteur scientifique.
Monatsh.	Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften.
Münch. Med. Wochenschr.	Munchener Medizinische Wochenschrift.
Nature	Nature.
Nuovo Cim.	Il nuovo Cimento.
Öfvers. K. Vet.-Akad. Forh.	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Pflüger's Archiv	Archiv fur die gesammte Physiologie des Menschen und der Thiere.
Pharm. Zentr.-h..	Pharmazeutische Zentralhalle.
Pharm. Post	Pharmazeutische Post.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie (1824–1877).
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Phil. Soc. Glasgow	Proceedings of the Royal Philosophical Society of Glasgow.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. Trav. chim.	Recueil des Travaux chimiques des Pay-Bas et de la Belgique.
Roy. Inst. Reports	Reports of the Royal Institution.
Schweigger's J.	Journal für Chemie und Physik.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.

ABBREVIATED TITLE.	JOURNAL.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zu Wien.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Techn. Jahresber.	Jahresbericht über die Leistungen der Chemischen Technologie.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trav. et Mém. du Bureau intern. des Poids et Mes.	Travaux et Mémoires du Bureau International des Poids et Mesures.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied Annalen	Wiedermann's Annalen der Physik und Chemie (1877–1899).
Wissenschaftl. Abhandl. phys.-tech. Reichsanst.	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Chem.	Kritische Zeitschrift für Chemie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genuss-m.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik, und Photochemie.

TABLE OF DATES OF ISSUE OF JOURNALS.

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year	Amer J Sci	Ann Chm Phys	Ann Min.	Arch Pharm.	Dingl. Poly. J	Gilbert's Annalen	J. Pharm. Chm.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800	.	(1) 32–35	...	...	.	4–6		5–8	90	..
1		36–39				7–9	...	8–11*	91	
2	.	40–43		...	. .	10–12	.	11–14	92	
3		44–47		.		13–15		14–17	93	
4		48–51			..	16–18	...	17–20	94	...
1805	.	52–55		.	.	19–21	...	20–23	95	
6		56–60	.	..	.	22–24	..	23–26	96	
7	...	61–64		.		25–27	...	26–29	97	...
8		65–68	..			28–30	.	29–32	98	...
9		69–72			...	31–33	(1) 1*	33, 34	99	. .
1810		73–76		...	...	34–36	2	35, 36	100	..
11	...	77–80	.	...	...	37–39	3	37, 38	101	...
12		81–84	. .		...	40–42	4	39, 40	102	. .
13	..	85–88		.		43–45	5	41, 42	103	..
14	...	89–92	..	. .		46–48	6	43, 44	104	...
1815		93–96	...	. .	..	49–51	(2) 1	45, 46	105	..
16	..	(2) 1–3		. .		52–54	2	47, 48	106	...
17		4–6	1, 2	...	. .	55–57	3	49, 50	107	
18		7–9	3	.	.	58–60	4	51, 52	108	...
19	(1) 1	10–12	4		.	61–63	5	53, 54	109	...
1820	2	13–15	5	...	1–3	64–66	6	55, 56	110	...
21	3	16–18	6	...	4–6	67–69	7	57, 58	111	...
22	4, 5	19–21	7	1, 2	7–9	70–72	8	59, 60	112	
23	6	22–24	8	3–6	10–12	73–75	9	61, 62	113	...
24	7, 8	25–27	9	7–10	13–15	76	10	63, 64	114	1, 2
1825	9	28–30	10, 11	11–14	16–18	Continued as Pogg. Annalen.	11	65, 66	115	3–5
26	10, 11	31–33	12, 13	15–19	19–22		12	67, 68	116	6–8
27	12	34–36	(2) 1, 2	20–23	23–26		13	(2) 1, 2	117	9–11
28	13, 14	37–39	3, 4	24–26	27–30		14	3, 4	118	12–14
29	15, 16	40–42	5, 6	27–30	31–34		15	5, 6	119	15–17

* First series known as *Bulletin de Pharmacie.*

Year.	Amer. J. Sci.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Bull. Soc. chim.	Compt. rend.	Dingl. Poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon.* scient.	Phil. Mag	Phil. Trans.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc	Sitzungsber. K. Akad. Wiss. Wien.
1830	17, 18	...	43-45	7-8	31-34	...	.	35-38	16	.	.	7, 8	120	18-20		...	
31	19, 20	...	46-48		35-39	...	...	39-42	17	..	...	9, 10	121	21-23	... 1	...	
32	21, 22	1-4	49-51	(3) 1, 2	40-43	...	...	43-47	18			11 (3) 1	122	24-26	2	...	
33	23, 24	5-8	52-55	3, 4	44-47	...	...	48-50	19			2, 3	123	27-30		...	
34	25-27	9-12	56-57	5, 6	48-50	...	...	51-54	20	1-3	...	4, 5	124	31-33		...	
1835	28, 29	13-16	58-60	7, 8	(2) 1-4	.	1	55-58	21	4-6	...	6, 7	125	34-36		...	
36	30, 31	17-20	61-63	9, 10	5-8	.	2, 3	59-62	22	7-9		8, 9	126	37-39	3	...	
37	32, 33	21-24	64-66	11, 12	9-12	.	4, 5	63-66	23	10-12		10, 11	127	40-42		...	
38	34, 35	25-28	67-69	13, 14	13-16	.	6, 7	67-70	24	13-15		12, 13	128	43-45		...	
39	36, 37	29-32	70-72	15, 16	17-20	.	8, 9	71-74	25	16-18	.	14, 15	129	46-48		...	
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41	40, 41	37-40	(3) 1-3	19, 20	25-28	...	12, 13	79-82	27	22-24		18, 19	131	52-54		...	
42	42, 43	41-44	4-6	(4) 1, 2	29-32	...	14, 15	83-86	(3) 1, 2	25-27		20, 21	132	55-57		...	
43	44, 45	45-48	7-9	3, 4	33-36	...	16, 17	87-90	3, 4	28-30		22, 23	133	58-60		...	
44	46, 47	49-52	10-12	5, 6	37-40	...	18, 19	91-94	5, 6	31-33		24, 25	134	61-63	4	...	
1845	48-50	53-56	13-15	7, 8	41-44	...	20, 21	95-98	7, 8	34-36		26, 27	135	64-66		1	
46	(2) 1, 2	57-60	16-18	9, 10	45-48	.	22, 23	99-102	9, 10	37-39	...	28, 29	136	67-69	...	1, 2	
47	3, 4	61-64	19-21	11, 12	49-52	.	24, 25	103-106	11, 12	40-42		30, 31	137	70-72		2, 3	
48	5, 6	65-68	22-24	13, 14	53-56	.	26, 27	107-110	13, 14	43-45		32, 33	138	73-75			1
49	7, 8	69-72	25-27	15, 16	57-60	.	28, 29	111-114	15, 16	46-48		34, 35	139	76-78			2, 3
1850	9, 10	73-76	28-30	17, 18	61-64	...	30, 31	115-118	17, 18	49-51	...	36, 37	140	79-81		3	4, 5
51	11, 12	77-80	31-33	19, 20	65-68	...	32, 33	119-122	19, 20	52-54		(4) 1, 2	141	82-84	5	4	6, 7
52	13, 14	81-84	34-36	(5) 1, 2	69-72	...	34, 35	123-126	21, 22	55-57		3, 4	142	85-87		5	8, 9
53	15, 16	85-88	37-39	3, 4	73-76	...	36, 37	127-130	23, 24	58-60		5, 6	143	88-90	6, 7	6	10, 11
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56	21, 22	97-100	46-48	9, 10	85-88	...	42, 43	139-142	29, 30	67-69	(1) 1	11, 12	146	97-99	8	9	19-22
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58	25, 26	105-108	52-54	13, 14	93-96	1	46, 47	147-150	33, 34	73-75	3	15, 16	148	103-105	9	11	28-33
59	27, 28	109-112	55-57	15, 16	97-100	2	48, 49	151-154	35, 36	76-78		17, 18	149	106-108	9, 10	12	34-38

* Often referred to by Series: Series 3, vols. 1-16, 1871-1886; Series 4, vols 1-24, 1887-1910; Series 5, vols. 1-9, 1911-1919 (one vol. yearly).

Year.	Amer. Chem. J	Amer. J. Sci.	Analyst.	Annalen.	Annalen Suppl.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem Trade J	Chem. Zeit.
1860		29, 30		113–116		58–60	17, 18	101–104		2	1, 2		
61		31, 32		117–120	1	61–63	19, 20	105–108		3	3, 4		
62		33, 34		121–124	2	64–66	(6) 1, 2	109–112		4	5, 6		
63		35, 36		125–128	2	67–69	3, 4	113–116		5	7, 8		
64		37, 38		129–132	3	(4) 1–3	5, 6	117–120		(2)1, 2	9, 10		
1865		39, 40		133–136	3, 4	4–6	7, 8	121–124		3, 4	11, 12		
66		41, 42		137–140	5	7–9	9, 10	125–128		5, 6	13, 14		
67		43, 44		141–144	6	10–12	11, 12	129–132		7, 8	15, 16		
68		45, 46		145–148		13–15	13, 14	133–136	1	9, 10	17, 18		
69		47, 48		149–152		16–18	15, 16	137–140	2	11, 12	19, 20		
1870		49, 50		153–156	7	19–21	17, 18	141–144	3	13, 14	21, 22		
71		(3)1, 2		157–160		22–24	19, 20	145–148	4	15, 16	23, 24		
72		3, 4		161–164	8	25–27	(7) 1, 2	149–150, 201	5	17, 18	25, 26		
73		5, 6		165–170		28–30	3, 4	201–203	6	19, 20	27, 28		
74		7, 8		171–174		(5) 1–3	5, 6	204, 205	7	21, 22	29, 30		
1875		9, 10		175–179		4–6	7, 8	206, 207	8	23, 24	31, 32		
76		11, 12	1	180–183		7–9	9, 10	208, 209	9	25, 26	33, 34		
77		13, 14	2	184–189		10–12	11, 12	210, 211	10	27, 28	35, 36		1
78		15, 16	3	190–194		13–15	13, 14	212, 213	11	29, 30	37, 38		2
79	1	17, 18	4	195–199		16–18	15, 16	214, 215	12	31, 32	39, 40		3
1880	1, 2	19, 20	5	200–205		19–21	17, 18	216, 217	13	33, 34	41, 42		4
81	2, 3	21, 22	6	206–210		22–24	19, 20	218, 219	14	35, 36	43, 44		5
82	3, 4	23, 24	7	211–215		25–27	(8) 1, 2	220	15	37, 38	45, 46		6
83	4, 5	25, 26	8	216–221		28–30	3, 4	221	16	39, 40	47, 48		7
84	5, 6	27, 28	9	222–226		(6) 1–3	5, 6	222	17	41, 42	49, 50		8
1885	6, 7	29, 30	10	227–231		4–6	7, 8	223	18	43, 44	51, 52		9
86	7, 8	31, 32	11	232–236		7–9	9, 10	224	19	45, 46	53, 54		10
87	9	33, 34	12	237–242		10–12	11, 12	225	20	47, 48	55, 56	1	11
88	10	35, 36	13	243–249		13–15	13, 14	226	21	49, 50	57, 58	2, 3	12
89	11	37, 38	14	250–255		16–18	15, 16	227	22	(3)1, 2	59, 60	4, 5	13

* Joining series 1 and 2 together. Also written as (3) 1, 2, 3, etc.

Phil. Mag	Nature.	Mon. scient. *	Monatsh	J. Soc. Chem. Ind.	J Russ. Phys. Chem. Soc	J. prakt. Chem.	J. Pharm. Chim.	J. Chem. Soc.	J. Amer. Chem. Soc.	Gazzetta.	Dingl. Poly. J.	Compt. rend.	Year
19, 20						79–81	37, 38				155–158	50, 51	1860
21, 22						82–84	39, 40				159–162	52, 53	61
23, 24		4				85–87	41, 42	15			163–166	54, 55	62
25, 26		5				88–90	43, 44	16			167–170	56, 57	63
27, 28		6				91–93	45, 46	17			171–174	58, 59	64
29, 30		7				94–96	(4) 1, 2	18			175–178	60, 61	1865
31, 32		8				97–99	3, 4	19			179–182	62, 63	66
33, 34		9				100–102	5, 6	20			183–186	64, 65	67
35, 36		10				103–105	7, 8	21			187–190	66, 67	68
37, 38	1	11			1	106–108	9, 10	22			191–194	68, 69	69
39, 40	1, 2, 3	12			2	(2) 1, 2	11, 12	23			195–198	70, 71	1870
41, 42	3, 4, 5	13			3	3, 4	13, 14	24		1	199–202	72, 73	71
43, 44	5, 6, 7	14			4	5, 6	15, 16	25		2	203–206	74, 75	72
45, 46	7, 8, 9	15			5	7, 8	17, 18	26		3	207–210	76, 77	73
47, 48	9, 10, 11	16			6	9, 10	19, 20	27		4	211–214	78, 79	74
49, 50	11, 12, 13	17			7	11, 12	21, 22	28		5	215–218	80, 81	1875
(5) 1, 2	13, 14, 15	18			8	13, 14	23, 24	29, 30		6	219–222	82, 83	76
3, 4	15, 16, 17	19			9	15, 16	25, 26	31, 32		7	223–226	84, 85	77
5, 6	17, 18, 19	20			10	17, 18	27, 28	33, 34		8	227–230	86, 87	78
7, 8	19, 20, 21	21			11	19, 20	29, 30	35, 36	1	9	231–234	88, 89	79
9, 10	21, 22, 23	22	1		12	21, 22	(5) 1, 2	37, 38	2	10	235–238	90, 91	1880
11, 12	23, 24, 25	23	2		13	23, 24	3, 4	39, 40	3	11	239–242	92, 93	81
13, 14	25, 26, 27	24	3	1	14	25, 26	5, 6	41, 42	4	12	243–246	94, 95	82
15, 16	27, 28, 29	25	4	2	15	27, 28	7, 8	43, 44	5	13	247–250	96, 97	83
17, 18	29, 30, 31	26	5	3	16	29, 30	9, 10	45, 46	6	14	251–254	98, 99	84
19, 20	31, 32, 33	27	6	4	17	31, 32	11, 12	47, 48	7	15	255–258	100, 101	1885
21, 22	33, 34, 35	28	7	5	18	33, 34	13, 14	49, 50	8	16	259–262	102, 103	86
23, 24	35, 36, 37	29, 30	8	6	19	35, 36	15, 16	51, 52	9	17	263–266	104, 105	87
25, 26	37, 38, 39	31, 32	9	7	20	37, 38	17, 18	53, 54	10	18	267–270	106, 107	88
27, 28	39, 40, 41	33, 34	10	8	21	39, 40	19, 20	55, 56	11	19	271–274	108, 109	89

Year.	Phil. Trans.	Pogg Annalen	Proc. Chem. Soc.	Proc. Roy Soc	Quarl. J. Chem. Soc	Rec. Trav. Chim.	Sitzungsber K Akad. Wiss. Wien	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. Kryst. Min	Zeitsch. physikal. Chem
1860	150	109–111		10, 11	13		39–42			1			
61	151	112–114		11	14		43, 44			2			
62	152	115–117		11, 12	Continued as J. Chem Soc.		45, 46			3			
63	153	118–120		12, 13			47, 48						
64	154	121–123		13			49, 50						
1865	155	124–126		14			51, 52			4			
66	156	127–129		15			53, 54			5			
67	157	130–132		15, 16			55, 56			6			
68	158	133–135		16, 17			57, 58			7			
69	159	136–138		17, 18			59, 60			8			
1870	160	139–141		18, 19			61, 62			9		1, 2	
71	161	142–144		19, 20			63, 64			10		2, 3	
72	162	145–147		20, 21			65, 66			11		3, 4	
73	163	148–150		21, 22			67, 68			12			
74	164	151–153		22, 23			69, 70			13			
1875	165	154–156		23, 24		1	71, 72		1, 2	14		4, 5	
76	166	157–159		24, 25		2	73, 74		3–5	15		5, 6	
77	167	160		25, 26		3	75, 76		6–8	16		6, 7	
78	168, 169	Continued as Wied. Annalen.		27, 28			77, 78			17		7, 8	
79	170			28, 29, 30			79, 80			18		8, 9, 10	
1880	171		1	30, 31		4	81, 82	1	9–11	19		10, 11	
81	172		2	31, 32, 33		5	83, 84	2	12–14	20		11, 12	
82	173		3	33, 34		6	85, 86	3	15–17	21		12, 13	
83	174		4	34, 35, 36		7	87, 88	4	18–20	22		13, 14, 15	
84	175		5	36, 37, 38		8	89, 90		21–23	23		15	
1885	176			38, 39			91, 92	5	24–26	24		10, 11	
86	177			40, 41			93, 94	6	27–29	25		11, 12	
87	A. 178			42, 43			95, 96	7	30–32	26		12, 13	1
88	179			43, 44, 45			97	8	33–35	27	1	13, 14, 15	2
89	180			45, 46, 47			98	9	36–38	28	2	15	3, 4

Compt. rend	Chem. Zeit.	Chem. Week-blad	Chem Trade J.	Chem News	Bull. Soc. chim	Ber.	Arch. Pharm.	Ann. Mines	Ann. Chim. Phys.	Annalen	Analyst.	Amer. J. Sci.	Amer. Chem. J.	Year
110, 111	14		6, 7	61, 62	3, 4	23	228	17, 18	19-21	256-260	15	39, 40	12	1890
112, 113	15		8, 9	63, 64	5, 6	24	229	19, 20	22-24	261-266	16	41, 42	13	91
114, 115	16		10, 11	65, 66	7, 8	25	230	(9) 1, 2	25-27	267-271	17	43, 44	14	92
116, 117	17		12, 13	67, 68	9, 10	26	231	3, 4	28-30	272-277	18	45, 46	15	93
118, 119	18		14, 15	69, 70	11, 12	27	232	5, 6	(7) 1-3	278-283	19	47, 48	16	94
120, 121	19		16, 17	71, 72	13, 14	28	233	7, 8	4-6	284-288	20	49, 50	17	1895
122, 123	20		18, 19	73, 74	15, 16	29	234	9, 10	7-9	289-293	21	(4) 1, 2	18	96
124, 125	21		20, 21	75, 76	17, 18	30	235	11, 12	10-12	294-298	22	3, 4	19	97
126, 127	22		22, 23	77, 78	19, 20	31	236	13, 14	13-15	299-303	23	5, 6	20	98
128, 129	23		24, 25	79, 80	21, 22	32	237	15, 16	16-18	304-309	24	7, 8	21, 22	99
130, 131	24	⋮	26, 27	81, 82	23, 24	33	238	17, 18	19-21	310-313	25	9, 10	23, 24	1900
132, 133	25	.	28, 29	83, 84	25, 26	34	239	19, 20	22-24	314-319	26	11, 12	25, 26	01
134, 135	26	4	30, 31	85, 86	27, 28	35	240	(10) 1, 2	25-27	320-325	27	13, 14	27, 28	02
136, 137	27	5	32, 33	87, 88	29, 30	36	241	3, 4	28-30	326-329	28	15, 16	29, 30	03
138, 139	28	6	34, 35	89, 90	31, 32	37	242	5, 6	(8) 1-3	330-337	29	17, 18	31, 32	04
140, 141	29	7	36, 37	91, 92	33, 34	38	243	7, 8	4-6	338-343	30	19, 20	33, 34	1905
142, 143	30	8	38, 39	93, 94	35, 36	39	244	9, 10	7-9	344-350	31	21, 22	35, 36	06
144, 145	31	9	40, 41	95, 96	(4) 1, 2	40	245	11, 12	10-12	351-357	32	23, 24	37, 38	07
146, 147	32	10	42, 43	97, 98	3, 4	41	246	13, 14	13-15	358-363	33	25, 26	39, 40	08
148, 149	33	11	44, 45	99, 100	5, 6	42	247	15, 16	16-18	364-371	34	27, 28	41, 42	09
150, 151	34	12	46, 47	101, 102	7, 8	43	248	17, 18	19-21	372-377	35	29, 30	43, 44	1910
152, 153	35	13	48, 49	103, 104	9, 10	44	249	19, 20	22-24	378-385	36	31, 32	45, 46	11
154, 155	36	14	50, 51	105, 106	11, 12	45	250	(11) 1, 2	25-27	386-394	37	33, 34	47, 48	12
156, 157	37	15	52, 53	107, 108	13, 14	46	251	3, 4	28-30	395-401	38	35, 36	49, 50	13
158, 159	38	16	54, 55	109, 110	15, 16	47	252	5, 6			39	37, 38	Publication ceased	14
160, 161	39		56, 57	111, 112	17, 18	48	253				40	39, 40		1915
162, 163	40		58, 59	113, 114	19, 20	49	254				41	41, 42		16
164, 165	41		60, 61	115, 116	21, 22	50	255	⋮	⋮	⋮	42	43, 44		17
166, 167	42		62, 63	117	23, 24	51					43	45, 46		18
168, 169	43		64, 65	118, 119	25, 26	52					44	47, 48		19

Phl Mag.	Nature	Mon. scient.*	Monatsh	J. Soc Chem. Ind	J. Russ Phys Chem. Soc	J. prakt. Chem.	J. Physical Chem	J. Pharm. Chim.	J. Ind. Eng. Chem.	J. Chem. Soc	J. Amer. Chem. Soc.	Gazzetta.	Dingl. Poly. J.	Year.
29, 30	41, 42	35, 36	11	9	22	41, 42		21, 22		57, 58	12	20	275–278	1890
31, 32	43, 44	37, 38	12	10	23	43, 44		23, 24		59, 60	13	21	279–282	91
33, 34	45, 46	39, 40	13	11	24	45, 46		25, 26		61, 62	14	22	283–286	92
35, 36	47, 48	41, 42	14	12	25	47, 48		27, 28		63, 64	15	23	287–290	93
37, 38	49, 50	43, 44	15	13	26	49, 50		29, 30		65, 66	16	24	291–294	94
39, 40	51, 52	45, 46	16	14	27	51, 52		(6) 1, 2		67, 68	17	25	295–298	1895
41, 42	53, 54	47, 48	17	15	28	53, 54		3, 4		69, 70	18	26	299–302	96
43, 44	55, 56	49, 50	18	16	29	55, 56		5, 6		71, 72	19	27	303–306	97
45, 46	57, 58	51, 52	19	17	30	57, 58		7, 8		73, 74	20	28	307–310	98
47, 48	59, 60	53, 54	20	18	31	59, 60		9, 10		75, 76	21	29	311–314	99
49, 50	61, 62	55, 56	21	19	32	61, 62	4	11, 12		77, 78	22	30	315	1900
(6) 1, 2	63, 64	57	22	20	33	63, 64	5	13, 14		79, 80	23	31	316	01
3, 4	65, 66	58	23	21	34	65, 66	6	15, 16		81, 82	24	32	317	02
5, 6	67, 68	59	24	22	35	67, 68	7	17, 18		83, 84	25	33	318	03
7, 8	69, 70	60, 61	25	23	36	69, 70	8	19, 20		85, 86	26	34	319	04
9, 10	71, 72	62, 63	26	24	37	71, 72	9	21, 22		87, 88	27	35	320	1905
11, 12	73, 74	64, 65	27	25	38	73, 74	10	23, 24		89, 90	28	36	321	06
13, 14	75, 76	66, 67	28	26	39	75, 76	11	25, 26		91, 92	29	37	322	07
15, 16	77, 78	68, 69	29	27	40	77, 78	12	27, 28		93, 94	30	38	323	08
17, 18	79–82	70, 71	30	28	41	79, 80	13	29, 30	1	95, 96	31	39	324	09
19, 20	82–85	72, 73	31	29	42	81, 82	14	(7) 1, 2	2	97, 98	32	40	325	1910
21, 22	85–88	74, 75	32	30	43	83, 84	15	3, 4	3	99, 100	33	41	326	11
23, 24	88, 89, 90	76, 77	33	31	44	85, 86	16	5, 6	4	101, 102	34	42	327	12
25, 26	90, 91, 92	78, 79	34	32	45	87, 88	17	7, 8	5	103, 104	35	43	328	13
27, 28	92, 93, 94	80, 81	35	33	46	89, 90	18	9, 10	6	105, 106	36	44	329	14
29, 30	94, 95, 96	82	36	34	47	91, 92	19	11, 12	7	107, 108	37	45		1915
31, 32	96, 97, 98	83	37	35	48	93, 94	20	13, 14	8	109, 110	38	46		16
33, 34	98, 99, 100	84	38	36		95, 96	21	15, 16	9	111, 112	39	47		17
35, 36	100–102	85	39	37		97, 98	22	17, 18	10	113, 114	40	48		18
37, 38	102–104	86	40	38		99, 100	23	19, 20	11	115, 116	41	49		19

* See footnote, p. xx.

Year	Phil. Trans.	Physikal. Zeitsch.	Proc. Chem. Soc.	Proc. Roy. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal Chem	Zeitsch. angew. Chem.	Zeitsch anorg. Chem.	Zeitsch. Elektro-Chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1890	A. 181	...	6	47, 48, 49	9	99	10	39–41	29	3	.	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	. 100	11	42–44	30	4			19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45–47	31	5	1, 2	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48–50	32	6	3, 4, 5	.	21, 22	11, 12
94	185	.	10	55, 56, 57	13	103	14	51–53	33	7	5–7	1	23, 24	13–15
1895	186	.	11	57, 58, 59	14	104	15	54–56	34	8	8–10	1, 2	24, 25	16–18
96	187, 188	.	12	59, 60	15	105	16	57–59	35	9	11, 12, 13	2, 3	26–28	19–21
97	189, 190	...	13	60, 61, 62	16	106	17	60–63	36	10	13–15	3, 4	28, 29	22–24
98	191	...	14	62, 63, 64	17	107	18	64–66	37	11	16–19	4, 5	29–31	25–27
99	192, 193	.	15	64, 65, 66	18	108	19	67–69	38	12	19–22	5, 6	31, 32	28–31
1900	194, 195	1	16	66, 67	19	109	20	Continued as Annalen der Physik.	39	13	22–25	6, 7	32–34	32–35
01	196, 197	2	17	68, 69	20	110	21		40	14	26–29	7	34–36	36–38
02	198, 199	3	18	69, 70	21	111	22		41	15	29–33	8	36, 37	39–42
03	200–202	4	19	71, 72	22	112	23		42	16	33–37	9	37–39	43–46
04	203	5	20	72, 73, 74	23	113	24		43	17	38–42	10	39, 40	47–49
1905	204, 205	6	21	74–76	24	114	25		44	18	43–48	11	40–42	50–53
06	206	7	22	A. 77, 78	25	115	26		45	19	48–52	12	42, 43	54–57
07	207	8	23	78, 79, 80	26	116	27		46	20	52–56	13	43, 44	58–60
08	207–209	9	24	80, 81	27	117	28		47	21	56–60	14	44–46	61–64
09	209, 210	10	25	82, 83	28	118	29		48	22	61–65	15	46, 47	65–69
1910	210	11	26	83, 84	29	119	30		49	23	65–69	16	48, 49	70–74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	69–73	17	49, 50	75–77
12	211, 212	13	28	86, 87	31	121	32		51	25	73–79	18	50–52	78–80
13	212, 213	14	29	88, 89	32	122	33		52	26	79–83	19	52, 53	81–86
14	213, 214	15	30	89, 90	33	123	34		53	27	84–90	20	54	86–88
1915	215, 216	16	Publication of matter of scientific interest now abandoned.	...	34	...	35		54	28	90–93	21	55	89, 90
16	216, 217	17		...	35	.	36		55	29	94–98	22	..	91, 92
17	217	18		...	36, 37	.	37		56	30	99–101	23	No issue*	92
18	217	...		.	37	.	38		57	31	102–104	24		92
19	...	...		...	38	.	39		58	32	105–109	25		

* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF

INORGANIC CHEMISTRY.

VOLUME III. PART I.

A TEXT-BOOK OF
INORGANIC CHEMISTRY.

VOL. III. THE ALKALINE EARTH METALS AND THEIR ASSOCIATES

PART I. THE ALKALINE EARTH METALS.

(SUBGROUP A.)

CHAPTER I.

INTRODUCTORY.

THE ELEMENTS OF ᴛ——ᴇᴄᴏɴᴅ GROUP CONSIDERED

GROUP II. forms the firs
electropositive metals of
metals of Group VII. T]
                                    hᵢ
                                ᴄ

Group II	
A Alkaline Earths	B. Zinc Group.
	Be
	Mg
Ca	Zn
Sr	C
Ba	
..	
Ra	

lithium aˈ
group, pᵩ
they resˈ
for exaᵣ
cannoᵗ

alkaline earth group or to the little subgroup, composed of the three remaining metals of Group II., zinc, cadmium, and mercury. They have, however, relationships with both groups.

Leaving out of account beryllium and magnesium, it is possible to make a much closer comparison between Groups I. and II. than between II. and III. The members of the A subgroup of Group I., consisting of the alkalies, elements closely resembling each other but becoming more electropositive with increasing atomic weight, exhibit certain features—notably the readiness with which they combine with oxygen and other electronegative elements, and the basic properties of their oxides—which are reproduced to a greater or less extent in the alkaline earths, the A subdivision of Group II. The latter also become increasingly electropositive with rise in atomic weight.

A further comparison may be drawn between the two B subgroups, copper, silver, and gold on the one hand, and zinc, cadmium, and mercury on the other. Both are much less electropositive than the A groups, the copper being more negative than the zinc group, and in both cases the elements become more electronegative with increase of atomic weight. In both also, insoluble oxides without alkaline properties are formed. In both A groups the sulphides are hydrolysed by water and in the B groups they are unaffected. The relationship between zinc and cadmium is much closer than between cadmium and mercury, and this is paralleled by the way in which gold stands apart from copper and silver. Owing to the presence of the rare earths in the third long period, there is

mercury atom, there are the mercurous salts formed apparently from a polymerised bivalent mercury molecule, Hg_2. It is, of course, the case that there are indications among some of the other metals of the existence of compounds similar to the mercurous salts, for example, $CaCl$ or Ca_2Cl_2, CaF or Ca_2F_2, and so on, but these are, in general, unstable and occur only among the halides and oxides. In addition, except in a very few instances, the evidence for their formation is not unimpeachable.

All the metals are more or less white. All except mercury are attacked by water under suitable conditions, but the alkaline earths much more readily than the others. All form refractory oxides which are very stable, with the exception of the oxides of mercury, which readily decompose to form the metal when heated. The cadmium and mercury oxides are coloured but the rest are white, zinc oxide being yellow when hot. All show a tendency to peroxide formation.

The soluble salts of all readily form double salts with one another and with salts of the alkali metals ; they also unite directly with varying numbers of molecules of ammonia forming ammoniates, which might be compared with the hydrates of the salts. Zinc and the alkaline earth metals also combine directly with ammonia, but these compounds are not to be classed with ammonium amalgam. Amides of the general formula $M(NH_2)_2$ are known in the case of calcium, strontium, barium, zinc, and cadmium.

Beryllium, zinc, cadmium, and mercury have a great tendency to form basic salts, a property shared to a certain extent by magnesium.

Hydrides of magnesium and the alkaline earths, except radium, are known, but not of zinc, cadmium, and mercury, whilst the existence of a beryllium hydride is doubtful. There are also carbides of beryllium, magnesium, and the alkaline earths, again excluding radium.

The tendency of beryllium oxide to show acid properties is seen again in a lesser degree in the oxides of zinc and cadmium.

Some of the solubility relationships are interesting. The fluorides of magnesium and the alkaline earths are insoluble, the others are soluble, with the exception of the mercury fluorides, which are very readily hydrolysed. Similar considerations apply to the sulphates, except that magnesium sulphate is soluble. The soluble sulphates are hydrated, and some of them show isomorphism, as also do the double sulphates formed from them.

The carbonates of the alkaline earths and magnesium are well-defined stable compounds, but it is difficult or impossible to obtain the carbonates of the other metals free from basic carbonate.

Zinc sulphide is soluble in acid, cadmium sulphide in concentrated but not in dilute acid, and mercury sulphide is insoluble in both. All the other sulphides are decomposed by water.

Nitrides of all the elements of the group are known, those of the alkaline earths, beryllium, magnesium, and, to a small extent, zinc, being formed by direct combination with nitrogen. Calcium and strontium are tarnished by nitrogen at ordinary temperatures.

Other compounds might be considered in the same way, but the above should be sufficient to indicate the relationships between the different members of the group.

A few of the physical constants are compared in the following table :—

Constant.	Be	Mg	Ca	Sr	Ba	Ra	Zn	Cd	Hg
Atomic number .	4	12	20	38	56	88	30	48	80
Atomic weight .	9·02	24·32	40·09	87·63	137·37	225·95	65·38	112 41	200 61
Approx. density .	1·84	1·74	1·54	2 63	3 78	..	6·92	8·65	13·6
Approx m.-pt. in °C.	1280	650	810	800	850	700	419	320	− 38·89
Approx. b.-pt. in °C.	..	1100	..	..	950	..	918	778	357
Heat of formation of chloride in Cal.	155	151	190·44	195·66	197 08	197·0 suggested value	97·14	93 0	HgCl$_2$53·3 Hg$_2$Cl$_2$62·65
M.-pt. of oxide in °C.	2450	2250	2572	3000	..	..	..	..	..
Heat of formation of oxide in Cal.	..	143 4	152	140	125 9	113·2 suggested value	80·29 to 84·7	57	HgO 21·4 Hg$_2$O22·2

COMPARATIVE STUDY OF THE ALKALINE EARTH METALS.

The inter-relations of the four alkaline earth metals, calcium, strontium, barium, and radium, may now be considered in somewhat greater detail. In general, leaving out of account the radioactive properties of radium, variations in the chemical and physical properties of these elements, or of their compounds, follow the same order as the atomic weights. It must, however, be remembered that, owing to the extreme rarity of the element, very few of the salts of radium have been

	Calcium.	Strontium.	Barium.	Radium.
Atomic weight.	40·09	87·63	137·37	225·95
Density of metal.	1·54	2·63	3·78	..
Specific heat of metal.	0·169	0·0742	0·068	..
Stability of hypochlorites.	Isolated in crystalline form.	Obtained mixed with a large proportion of chloride and chlorate.	Very unstable.	..
Sublimation temperature of bromides, ° C.	720	770	820	Less volatile than barium bromide
Colour of carbide crystals.	Colourless.	Brown-red.	Black.	..
Density of carbide.	2·22	3·19	3·75	..
Density of nitrate.	2·24–2·50	2·98	3·22	..

carefully examined, nor has there been much opportunity for the study of the metal itself. There is, nevertheless, every reason to suppose that, chemically, radium closely resembles barium. It has been observed, for example, that, when precipitated microchemically, a number of its salts appear to be isomorphous with the corresponding barium salts.

The four metals are all silvery white and fairly soft. At ordinary temperatures they readily react with various gases, such as oxygen, nitrogen, and the halogens, and also with acids and water, the chemical reactivity increasing with the atomic weight. They are, therefore, all difficult to prepare in the pure state; calcium, being the least electro-positive, is obtained the most easily.

The heats of formation of the halides increase from calcium to barium, except in the case of the fluorides, where the reverse rule holds, as it also does for the oxides. The heats of formation of the peroxides from the ordinary oxides, on the other hand, become greater with increasing atomic weight, with the result that barium peroxide is more easily prepared than the peroxides of either strontium or calcium. The

	Calcium	Strontium.	Barium.	Radium.
Heat of formation of fluoride, Cal.	239·18	237·02	226·68	(225) [1]
Heat of formation of chloride, Cal.	190·44	195·66	197·08	(197)
Heat of formation of bromide, Cal.	169·2	176·5	179·82	(180)
Heat of formation of iodide, Cal.	141	147·5	149·9	(151·6)
Heat of formation of oxide, Cal.	152	140	125·9	..
Heat of formation of peroxide from oxide and oxygen, Cal.	5·43	10·875	12·1	..

heat of hydration of the oxide to the hydroxide increases from calcium to barium, and corresponding with this, the dissociation temperatures rise in the same order. The hydroxides become more soluble as the

	Calcium.	Strontium.	Barium.	Radium.
Heat of hydration of oxide, Cal.	15·33	19·44	24·24	..
Dissociation temperature of hydroxide, ° C.	547	778	998	..
Solubility of hydroxide, gram-equivalents per litre.	0·044	0·133	0·47	..

[1] The numbers in brackets have not been determined experimentally, but were predicted by de Forcrand from a consideration of the general relationships between members of the alkaline earth group, *Ann. Chim. Phys.,* 1911, [8], **24,** 256 ; *Compt. rend.,* 1911, **152, 66.**

atomic weight increases, and there is also a change in alkalinity in the same direction.   All three form tetroxides of the general formula $MO_2.O_2$, probably comparable with the polysulphides.

The heats of solution of the chlorides, bromides, and iodides all decrease with increasing atomic weight of the element, and at the same time the salts become less deliquescent.   In each case the deliquescence increases from the chloride to the iodide, barium chloride being practically non-deliquescent.   The hexahydrates of calcium and strontium chlorides are isomorphous, but the existence of a hexahydrate of barium chloride is very doubtful.   The chlorides, bromides, and iodides resemble each other in the readiness with which they form double salts, as well as addition compounds, with ammonia and substituted ammonias.

	Calcium.	Strontium.	Barium.	Radium.
Heat of solution of chloride, Cal.	17·48	11·14	1·92	(0)
Heat of solution of bromide, Cal.	24·51	16·1	4·98	(2)
Heat of solution of iodide, Cal.	28·12	20·5	10·3	(6·4)

The fluorides, in contrast to the other halides, are not very soluble, the solubility rising from calcium to barium.   The solubility of the sulphates runs in the opposite direction.   The solubility of radium sulphate has also been examined, and the salt evidently falls into line with the other sulphates, since it is an extraordinarily insoluble compound.

	Calcium.	Strontium.	Barium.	Radium.
Temperature, ° C. . .	18	18	18	25
Solubility of fluoride, milli-equivalents per litre.	0·417	1·86	18·3	..
Solubility of sulphate, milli-equivalents per litre.	29·5	1·245	0·0190	0·00013

The heats of formation of the hydrides, following the order of stability, diminish from calcium to barium, whilst the heats of formation of the nitrides probably become greater.   The hexammonium compounds of the metals, or the hexammoniates, show a slight decrease of the heat of formation in the direction of increasing atomic weight.   The stability of the carbonates follows the same order as the stability of the hydroxides, since it is extremely hard to drive off the carbon dioxide from barium carbonate.

The volatile salts of the alkaline earths all colour the Bunsen flame, a red flame of varying degrees of purity being given by calcium, strontium, and radium, whilst barium differs in giving a green flame.

Isomorphism occurs in many cases between the "corresponding"

	Calcium.	Strontium	Barium.	Radium.
Heat of formation of hydride, Cal.	45·1	38·4	37·5	(35·4)
Heat of formation of nitride, Cal.	111·2	..	149·4	..
Heat of formation of hexammoniate, Cal.	10·32	9·90	9·68	..
Dissociation temperature of carbonate, ° C.	898	1155	1350	..

or " analogous" salts of the different elements : for example, the azides are isomorphous, the nitrites, and also the bromates—barium chlorate and iodate in addition being isomorphous with the bromates. The α-forms of the sulphates are isomorphous and miscible in all proportions above 1152° C. Below that temperature, however, strontium sulphate is miscible with barium sulphate, but only partially miscible with calcium sulphate.

All the alkaline earth metals, in the form of their compounds, are very widely distributed, but there is a striking difference between the amounts of each present in the earth's crust, calcium compounds, especially the carbonate, being present in very large quantities, whilst radium is only found in extremely minute amounts. Strontium and barium, especially the former, are not found in very large quantities.

As regards the physiological action of the compounds of the alkaline earth metals, calcium is of vital importance to both the animal and the vegetable organism; barium, on the other hand, is strongly toxic, whilst strontium has very little effect. It would scarcely be possible to determine the action of radium due to its purely chemical characteristics, since at any effective concentration of the element this would be entirely superseded by the influence of the radiation. From the latter point of view, of course, radium has already shown itself to be of great service to medical science.

CHAPTER II.

CALCIUM AND ITS COMPOUNDS.

CALCIUM.

Symbol, Ca. Atomic weight, 40·07 (O=16).

Occurrence.—Calcium, always in the combined form, is among the more widely distributed and the more abundant of the elements. It is an important constituent of many rocks, both igneous and sedimentary, occurring chiefly as carbonate, sulphate, silicate, phosphate, and fluoride. There are, in fact, whole ranges of mountains composed largely of calcium carbonate. Calcium is also a common mineral ingredient of most natural waters. Finally, animal skeletons owe their rigidity mainly to calcium phosphate, and the shells of molluscs and of birds' eggs to the carbonate.

The metal forms 3·47 per cent. of the older or primitive part of the earth's crust,[1] or 3·25 per cent. of the outer part of the earth, including crust and sea.[2] The amount of calcium in sea-water is from 0·03 per cent. to 0·05 per cent.[3]

Calcium has also been found in meteorites,[4] and by spectral analysis in the sun and fixed stars.

The chief calcium minerals, together with their more important physical constants, are given in the table on the following page.

History.—Compounds of calcium have been employed for building purposes since very early times. A mortar composed of sand and either lime or burnt gypsum was used by the Egyptians, and in the first century A.D. Dioscorides and Pliny described lime-burning and slaking. In 1693 Homberg heated together sal-ammoniac and lime for the production of Homberg's phosphorus, a phosphorescent calcium chloride. In 1722 Hofmann showed that lime was a distinct earth. Black noted its alkalinity in 1755.[5] Lime was regarded as a simple body until the time of Lavoisier, who suspected it to be an oxide. The metal was isolated by Davy[6] in 1808, and independently by Berzelius and Pontin.

Preparation of Calcium.—The methods by which the problem of

[1] Clarke, "The Data of Geochemistry," *Bull. U.S. Geol. Survey*, No. 616, 34.

[2] Vogt, *Zeitsch. prakt. Geol.*, 1898, 225, 314, 377, 413 ; 1899, 10. See A. Geikie, *Text-book of Geology* (Macmillan & Co., Ltd.), 1903, vol. i., p. 83.

[3] Dittmar, *Rep. of Voyage of "Challenger,"* vol. i., "Physics and Chemistry," 1884, p. 203, *et seq.* ; Wheeler, *J. Amer. Chem. Soc.*, 1910, 32, 646.

[4] Smith, *Ann. Chim. Phys.*, 1879, [5], 16, 467 ; Farrington, *Meteorites* (R. R. Donnelley & Sons Co., Chicago), 1915, p. 113.

[5] Black, *Alembic Club Reprints*, No. 1.

[6] Davy, *Phil. Trans.*, 1808, 98, 341.

the separation of metallic calcium has been attacked may be divided into two classes :—

    I. Electrolysis of a fused compound.

    II. The displacement of calcium from its compounds by a more electropositive metal.

Only the first has risen to the dignity of a commercial process, and that not to any great extent, owing to the limited use to which the metal has hitherto been put.

Electrolytic Methods.—Davy electrolysed a paste of calcium oxide mixed with the red oxide of mercury, using a platinum anode and a

Mineral.	Chemical Composition.	Density.	Hardness (Mohs' Scale).	Crystallographic System.
Actinolite	$Ca(Mg,Fe)_3[SiO_3]_4$	3 03–3 17	5–6	Monoclinic.
Alstonite	$(Ba,Ca)CO_3$	3 65–3 76	4–4 5	Rhombic.
Anhydrite	$CaSO_4$	2 9–3	3–3 5	Rhombic.
Ankerite	$(Ca,Mg,Fe)_2[CO_3]_2$	2 95–3 1	3 5–4	Hexagonal.
Anorthite	$CaAl_2Si_2O_8$	2 73–2 76	6	Triclinic.
Apatite	$Ca_5(Cl,F,(OH))[PO_4]_3$	3·17–3 23	5	Hexagonal.
Aragonite	$CaCO_3$	2 9–3	3·5–4	Rhombic.
Borocalcite	$CaB_4O_7.4H_2O$	..	..	..
Brushite	$HCaPO_4.2H_2O$	2·21	2–2 5	Monoclinic.
Calcspar (calcite)	$CaCO_3$	2 6–2 8	3	Hexagonal.
Colemannite	$Ca_2B_6O_{11}.5H_2O$	2 42	3 5–4·5	Monoclinic.
Diopside	$Ca(Mg,Fe)[SiO_3]_2$	3·2–3 38	5–6	Monoclinic.
Dolomite	$(Ca,Mg)CO_3$	2 85–2 95	3·5–4 5	Hexagonal.
Fluorspar (fluorite)	CaF_2	3 1–3·2	4	Cubic.
Gypsum (selenite)	$CaSO_4.2H_2O$	2·2–2 4	1·5–2	Monoclinic.
Pandermite	$Ca_2B_6O_{11}.3H_2O$	2·26–2·48	3	Monoclinic.
Scapolite	$Ca_4Al_6Si_6O_{25}$	2·72	5·5–6	Tetragonal.
Scheelite	$(Ca,Mo)WO_4$	5·9–6·1	4·5–5	Tetragonal.
Tachydrite	$CaMg_2Cl_6,12H_2O$	1 66	..	Hexagonal.
Wollastonite	$CaSiO_3$	2·8–2 9	4·5–5	Monoclinic.

mercury cathode. An amalgam was formed from which distillation in a current of hydrogen failed to remove the mercury completely.[1] Several subsequent investigators attempted the separation by similar methods with more or less success.[2]

The experiments of Borchers and Stockem [3] first made possible the production of metallic calcium on a large scale.[4] They electrolysed used calcium chloride, avoiding a temperature above the melting-point

[1] Davy, *loc. cit.*

[2] Hare, *J. prakt. Chem.*, 1840, [1], **19**, 249 ; 1841, [1], **22**, 383 ; Bunsen, *Pogg. Annalen*, 1854, **91**, 619 ; Matthiessen, *Annalen*, 1855, **93**, 277 ; *J. Chem. Soc.*, 1855, **8**, 27 ; Frei, *Annalen*, 1876, **183**, 367 ; von Lengyel, *Chem. Zentr.*, 1898, ii, 262 ; Moissan, *Ann. Chim. Phys.*, 1899, [7], **18**, 289 ; Ruft and Plato, *Ber.*, 1902, **35**, 3612.

[3] Borchers and Stockem, *Zeitsch. Elektrochem.*, 1902, **8**, 757, 938 ; *Ber.*, 1903, **36**, 17.

[4] Rathenau, *Zeitsch. Elektrochem.*, 1904, **10**, 508.

of calcium at the cathode because the molten metal dissolves in calcium chloride, producing the subchloride Ca_2Cl_2. The product obtained round the cathode submerged below the surface of the liquid, was spongy, brittle, and not very pure.

Redlich and Suter [1] obtained a much more compact product by a device which has been adopted in the commercial production of calcium at Bitterfeld by the firm of Siemens and Halske. Calcium chloride, sometimes mixed with calcium fluoride to reduce the temperature of fusion, is used. As calcium burns in air above 800° C., this forms the limit beyond which the temperature must not be allowed to rise. The cathode, a cooled iron rod just touching the surface of the liquid, is gradually raised as electrolysis proceeds, drawing with it the solid calcium protected by a layer of the fused salt. This contact cathode tends to prevent the formation of a "metallic fog," or suspension of finely divided metallic calcium. The current density required at the cathode is about 100 amp. per sq. cm. The metal is obtained in the form of irregular cylinders weighing 200 to 300 grm. The following percentage analysis of Bitterfeld calcium has been given : [2] Ca 97·75, Mg 0·89, Si 0·84, Fe 0·14, Al 0·37. It may, however, reach a purity of 99·3–99·6 per cent.[3] Further purification of the commercial product may be effected by distillation in a high vacuum.[4]

Subsequent study of the electrolytic separation of the metal has been mainly concerned with the relative merits of the submerged and contact cathodes, and with the desirability or otherwise of adding another electrolyte to the calcium chloride. Goodwin [5] at first adopted a submerged cathode of wrought iron passing through the bottom of a furnace of Acheson graphite, the walls of which formed the anode. Eventually he replaced this by the contact electrode employed at Bitterfeld, and that appears to be the most satisfactory method.[6]

Goodwin used fused calcium chloride alone for the bath, but Moldenhauer and Andersen [7] used potassium chloride in place of the calcium fluoride of the commercial process, and with a current density of 60–110 amp. per sq. cm. obtained metallic calcium practically free from potassium, with a current efficiency of 75–90 per cent. Brace [8] concluded that pure, completely dehydrated calcium chloride is better than any admixture with another electrolyte. He also found that careful control of the temperature is necessary, and can be secured by varying the separation and degree of immersion of the anodes. Almost the entire charge of the electrolyte should be molten, only a small portion at the sides and bottom of the graphite container being allowed to remain solid.[9]

[1] Redlich and Suter, English Patent, 20655, Sept. 25, 1903 ; Rathenau, loc. cit.

[2] Setlik, Chem. Zeit., 1905, 11, 612.

[3] Moissan and Chavanne, Compt. rend., 1905, 140, 122. See also Muthmann, Weiss, and Metzger, Annalen, 1907, 355, 137.

[4] Biltz and Hohorst, Zeitsch. anorg. Chem., 1921, 121, 1.

[5] Goodwin, J. Amer. Chem. Soc., 1903, 25, 873 ; 1905, 27, 1403. Proc. Amer. Phil. Soc. (Philadelphia), 1904, 43, 381. See also v. Kügelgen, Zeitsch. Elektrochem., 1908. 24, 143.

[6] Tucker and Whitney, J. Amer. Chem. Soc., 1906, 28, 84 ; Brace, Engineering, 1921, 111, 308.

[7] Moldenhauer and Andersen, Zeitsch. Elektrochem., 1913, 19, 444.

[8] Brace, loc. cit.

[9] See also Frary, Bicknell, and Tronson, Trans. Amer. Electrochem. Soc., 1910, 18, 117 ; Chem. Zentr., 1911, i, 1345 ; Johnson, Trans. Amer. Electrochem. Soc., 1910, 18, 125 ; J. Soc. Chem. Ind., 1910, 29, 1389 ; Rideal, Industrial Electrometallurgy (Baillière, Tindall & Cox), 1918, p. 120.

Wohler [1] described the conditions under which the metal may be prepared on a laboratory scale. He used a mixture of 100 parts of calcium chloride with 12 parts of calcium fluoride, melting at 660° C., and contained in an iron vessel. The cathode was an iron wire of 8 mm. diameter, and a current of 40 amp. at 38 volts was supplied, giving a density of 100 amp. per sq. cm. of cathode surface.

It is also possible to obtain calcium by electrolysis of a concentrated solution of calcium chloride, instead of the fused salt, using a mercury cathode. The amalgam may then be distilled.[2]

Displacement or purely Chemical Methods.—These consist essentially in the replacement of calcium in its salts by a more electropositive metal. In the first attempts, in which, for example, calcium iodide was heated with sodium,[3] or with sodium and zinc,[4] or calcium iodide was replaced by a mixture of potassium iodide and calcium chloride,[5] the pure product was never obtained.

Moissan [6] succeeded in getting rid of excess of sodium by utilising the fact that, although it dissolves calcium at red heat, the two metals are not miscible at crystallising-point, and the sodium can be removed by treatment with absolute alcohol, leaving the calcium untouched in the form of brilliant white crystals of 98·9–99·2 per cent. purity. It was necessary to avoid contact with oxygen, hydrogen, or nitrogen, and to use pure salts. The fact that the process required sodium and large quantities of absolute alcohol prevented its use commercially.

The difficulties of the displacement method are due largely to the circumstance that, although calcium is less electropositive than sodium at ordinary temperatures, at a temperature of about 800° C., or even lower, it will liberate sodium from its compounds,[7] due either to the greater volatility of sodium at higher temperatures, or to calcium becoming more electropositive than sodium. It will not, however, replace potassium. At bright red heat a mixture of calcium and potassium is obtained.[8]

Other reducing agents have been suggested in place of sodium—for example, magnesium,[9] carbon,[10] and aluminium.[11] Methods have also been proposed for the direct production of calcium alloys, but these will be referred to later.

Physical Properties.—Calcium crystallises in hexagonal or rhombohedric plates, which, when freshly cut, have a bright silver-white appearance.[12] X-ray analysis shows that the calcium atoms are arranged as a face-centred cube, each being surrounded by twelve equi-distant

[1] Wöhler, *Zeitsch. Elektrochem.*, 1905, 11, 612.

[2] Brace, *J. Inst. Metals*, 1921, 25, 161.

[3] Liès-Bodart and Jobin, *Ann. Chim. Phys*, 1858, [3], 54, 363; *Compt. rend.*, 1858 47, 23. See also Dumas, *ibid.*, 1859, 49, 575.

[4] Caron, *Compt. rend.*, 1859, 48, 440; 1860, 50, 547; *Annalen*, 1859, 111, 114; 1860 115, 355.

[5] Sonstadt, *Chem. News*, 1864, 9, 140.

[6] Moissan, *Compt. rend.*, 1898, 126, 1753.

[7] de Forcrand, *ibid.*, 1911, 152, 27.

[8] Daneel and Stockem, *Zeitsch. Elektrochem.*, 1905, 11, 209.

[9] Winkler, *Ber.*, 1890, 23, 120.

[10] Moissan. *Ann. Chim. Phys.*, 1899, [7], 18, 289.

[11] Weston and Ellis, *Trans. Faraday Soc.*, 1908, 4, 130.

[12] Moissan, *Compt. rend.*, 1898, 127, 584.

atoms.[1] The diameter of the atoms—that is, the distance from centre to centre of contiguous atoms—is $3\cdot40 \times 10^{-8}$ cm.[2]

Calcium is malleable and can be drawn into wire of $\frac{3}{10}$ mm. diameter. The hardness is $2\cdot2$–$2\cdot5$ on Mohs' scale   that is, between lead and Iceland spar,[3] or about equal to that of aluminium.[4] The tensile strength is 612 kgm. per sq. cm.[4]

The following values have been given for the specific electrical resistance: $3\cdot43 \times 10^{-6}$ ohms per c.c. at $0°$ C., temperature coefficient $0\cdot00457$; [1] $4\cdot6 \times 10^{-6}$ ohms per c.c. at ordinary temperature, increasing linearly up to about $13\cdot6 \times 10^{-3}$ ohms at $600°$ C., with a temperature coefficient of $0\cdot00364$; [5] $6\cdot77 \times 10^{-3}$ ohms per c.c. at ordinary temperature.[6]

Swisher also determined the thermo-electric power to be positive with respect to lead, the potential varying from $8\cdot9$ microvolts per degree at $50°$ C., to $14\cdot0$ microvolts at $400°$ C.

Calcium has two resonance potentials : $1\cdot90$ volts, the wave-length determining it being $6572\cdot78$ Å ; and $2\cdot85$ volts, wave-length $4226\cdot73$ Å. The ionisation potential is $6\cdot1$ volts, and the corresponding wave-length $2027\cdot56$ Å.[7] McLennan and Young [8] found $6\cdot12$ volts for the ionisation potential and $\lambda = 2028\cdot2$ Å.

The ionic mobility of $\frac{1}{2}Ca^{\cdot}$ is 51.[9]

Using a dropping mercury cathode, Heyrovský showed the deposition potential of the calcium ion to be $-2\cdot023$ volts.[10]

The photo-electric emission of electrons by calcium is normal over wave-lengths 2300 Å to 7000 Å, and has a maximum value at $\lambda = 3650$ Å. This maximum becomes more pronounced as the angle of incidence diminishes.[11]

When heated, calcium becomes positively charged.[12]

The density of calcium appears to be in the neighbourhood of $1\cdot54$.[13] Higher values given by earlier investigators are evidently due to impurities, which will, for the most part, be heavier than calcium. For the redistilled metal Arndt obtained the value $1\cdot52$,[14] and Biltz and Hohorst $1\cdot542$ at $25°$ C.[15]   Brace [16] found $1\cdot46$ for the density of the cold rolled material at $22°$ C.

The melting-point of calcium is $810°$ C.,[17] but it will sublime below

[1] Hull, *Science*, 1920, 52, 227 ; *Chem. Abs.*, 1920, 14, 3363.

[2] Bragg, *Phil. Mag.*, 1920, [6], 40, 169. Calculation from the ionisation potential gives $2\ 36 \times 10^{-8}$ cm. ; see Saha, *Nature*, 1921, 107, 682.

[3] Ruff and Plato, *Ber.*, 1902, 35, 3612.

[4] Goodwin, *Proc. Amer. Phil. Soc.* (Philadelphia), 1904, 43, 381 ; *Chem. Zentr.*, 1905, ii, 1154.

[5] Swisher, *Phys. Review*, 1917, [2], 10, 601.

[6] Brace, *J. Inst. Metals*, 1921, 25, 153. Calculation from Ruff and Plato's value for conductivity gives $10\ 5 \times 10^{-6}$ at $20°$ C., and from Matthiessen's $7\cdot7 \times 10^{-6}$ ohms at $17°$ C.

[7] Mohler, Foote, and Stimson, *Phil. Mag.*, 1920, [6], 40, 73.

[8] McLennan and Young, *Proc. Roy. Soc.*, 1919, [A], 95, 273.

[9] Kohlrausch, *Zeitsch. Elektrochem.*, 1907, 13, 343 (footnote).

[10] Heyrovský, *Phil. Mag.*, 1923, 45, 303.

[11] Pohl and Pringsheim, *Ber. Deut. physikal. Ges.*, 1913, 15, 111; see also Case, *Phys. Review*, 1921, [2], 17, 398.

[12] Horton, *Proc. Roy. Soc.*, 1907, [A], 79, 96.

[13] Goodwin, *loc. cit.* ; Moissan and Chavanne, *Compt. rend.*, 1905, 140, 122.

[14] Arndt, *Ber.*, 1904, 37, 4733.

[15] Biltz and Hohorst, *Zeitsch. anorg. Chem.*, 1922, 121, 1.

[16] Brace, *loc. cit.*

[17] Moissan and Chavanne, *loc. cit.* ; Arndt, *loc. cit.* See also Tamaru, *Zeitsch. anorg. Chem.*, 1909, 62, 81 ; Ruff and Plato, *Ber.*, 1902, 35, 3612

the melting-point and is very volatile above it.[1] It is more volatile than either barium or strontium. The vapour pressure of calcium at the melting-point is 2 mm., and, by calculation from the vapour-pressure curve, the boiling-point is 1240° C.[2]

The following values have been given for the specific heat :— .

Specific Heat.	Temperature Range, ° C.	Authority.
0 1453	0 — 20 5	
0·147	0 — 78	
0 149	0 — 100	Bernini, *Physikal. Zeitsch.*, 1907, **8**, 150.
0·152	0 — 157	
0 1704	0 — 100	Bunsen, *Pogg. Annalen*, 1870, **141**, 1.
0 157	- 185 to +20	Nordmeyer and Bernoulli, *Ber. Deut. physikal. Ges.*, 1907, **5**, 175.

More extensive specific heat investigations have been carried out by Eastman and Rodebush,[3] employing Nernst's method for low temperatures. The specific heat at −205·4° C. is 0·098, corresponding to an atomic heat of 3·93, and this value gradually increases with temperature until, at 20·5° C., the value 0·169, atomic heat 6·75, is reached.

The most intense lines in the spectrum of calcium, measured in Ångstrom units, are the following[4] : —

Arc : Ultra-violet : 2197·791, 2208·606, 3006·864, 3158·877, 3361·918, 3644·400 ; Visible : 3706·022, 3933·68, 3968·482, 4226·731, 4283·008, 4302·527, 4425·428, 4434·947, 4454·765, 4585·868, 5265·559, 5349·470, 5588·746, 5857·476, 6162·177, 6439·086, 6462·576, 6493·789, 6572·783 ; Infra-red : 8499·3, 8542·6, 8662·6, 10345·0.

Spark : Ultra-violet : 2197·94, 2208·83, 2398·61, 3158·864, 3179·345 ; Visible : 3933·67, 3968·476, 4226·730, 4283·004, 4289·361, 4298·985, 4302·523, 4435·960, 4454·780.

The X-ray spectrum of calcium has been studied by Moseley.[5]

Chemical Properties.—Calcium is a highly electropositive element, and combines directly with non-metals, although Goodwin[6] considers that it is more inert than is generally supposed. In many cases reaction takes place with considerable vigour. For example, if calcium and fluorine are brought together at ordinary temperatures, the rate of

[1] Wöhler and Rodewald, *Zeitsch. physikal. Chem.*, 1908, **61**, 68.
[2] Pilling, *Phys. Review*, 1921, **18**, 362 ; *J. Inst. Metals*, 1921, **25**, 170. See also Hirsch and Aston, *Trans. Amer. Electrochem. Soc.*, 1908, **13**, 143 ; Walden, *Zeitsch. anorg. Chem.*, 1920, **112**, 231.
[3] Eastman and Rodebush, *J. Amer. Chem. Soc.*, 1918, **40**, 489.
[4] Marshall Watts, *Index of Spectra* (Wesley & Son, London ; Abel Heywood & Son, Manchester), Appendices " V " (1913), " W " (1914), and " X " (1917). See also *Tables Annuelles de Constantes et Données Numériques* (Gauthier-Villars et Cie, Paris), 1913–1916, vol. iv, pp. 384, 388, 390, and 391.
[5] Moseley, *Phil Mag.*, 1913, [6], **26**, 1028.
[6] Goodwin, *loc. cit.*

reaction is sufficiently great to raise the mass to incandescence, and the resulting fluoride is molten.[1]

The readiness with which calcium combines with the nitrogen of the air, forming a yellow coating over the surface, resulted in an error in the description of the colour of the metal by the earlier investigators,[2] the pure untarnished metal being silvery white in appearance.

At 300° C. it burns in oxygen with a brilliant light and an intense heat, which volatilises the lime. Combination with the other halogens, with hydrogen, and with sulphur, selenium, tellurium, phosphorus, antimony, boron, and silicon, can also be effected with varying facility.

Dilute acids are decomposed by calcium with vigorous evolution of hydrogen. Water is attacked more slowly owing to the formation of an insoluble coating of hydroxide on the surface. Carbon dioxide, silica, fuming sulphuric acid, sulphuretted hydrogen, borates, oxides, sulphides, many fused salts, and various organic compounds may also be decomposed.[1] Calcium will even decompose some alkali salts at bright red heat.[3]

Moisture appears to have the customary influence, since calcium is unaffected by dry oxygen.[4]

The reactivity of calcium depends largely on its physical state. The fused mass of the metal is less readily attacked than the well-defined crystals.[5] Sieverts [6] showed that some samples of commercial calcium combine with nitrogen only above 800° C., but the majority have a second temperature range of activity between 300° and 660° C., the optimum temperature being 440° C. The inactive calcium may be changed to the active form by melting, and then cooling slowly to produce a relatively coarse-grained crystalline structure. It will then absorb nitrogen even between 150° and 300° C. The reverse change from the active to the inactive modification may be brought about by chilling quickly from 840° C. or by mechanical powdering. The absorption of hydrogen also depends on crystalline structure, but no samples are quite indifferent to hydrogen below 800° C.

Calcium reacts with gaseous ammonia, or dissolves in liquid ammonia to form an addition compound which gradually gives off ammonia and hydrogen at room temperature and forms an amide.[1]

With alcoholic ammonia it forms calcium ethylate, the amide probably being an intermediate product.[7]

Physiological Action of Calcium.—The salts of calcium are not in general toxic, but in large quantities will act as muscular poisons.[8] As calcium is a necessary constituent of bones, a deficiency of calcium

[1] Moissan, Compt. rend., 1898, 127, 584 ; Ann. Chim. Phys., 1899, [7], 18, 289.
[2] von Lengyel, Chem. Zentr., 1898, ii, 262.
[3] See paragraph on preparation of calcium by displacement methods.
[4] Erdmann and van der Smissen, Annalen, 1908, 361, 32.
[5] Moissan and Chavanne, Compt. rend., 1905, 140, 122. See also Doormer, Zeitsch. anorg. Chem., 1906, 49, 362.
[6] Sieverts, Chem. Zeit., 1915, 39, 804 ; Zeitsch. angew. Chem., 1915, 28, [3], 619 ; Zeitsch. Elektrochem., 1916, 22, 15. According to Ruff and Hartmann, Zeitsch. anorg. Chem., 1922, 121, 167, the behaviour of calcium towards nitrogen depends less on its physical state than on its chemical purity, pure calcium being practically unaffected by nitrogen below the melting-point. (See Nitride.)
[7] Doby, Zeitsch. anorg. Chem., 1903, 35, 93.
[8] Rabuteau and Ducoudray, Compt. rend., 1875, 76, 349.

in the diet induces a rachitic condition.[1] The amount of lime required by the growing mammal is at least 1·2 per cent. of the increase in bodily weight. The effects of a deficiency are limited to the skeleton and, perhaps, the brain. The bones do not weigh less, but contain less organic matter and ash and more water.[2] The blood also contains calcium, the average quantity under normal conditions being 6·1 mgm. per 100 c.c. for males and 7·1 for females.[3]

Calcium is necessary to the growth of plants, and is found especially in the leaves.[4] In general, the salts, especially the iodide, are more toxic for plants than for animals ; not so, however, the sulphate, carbonate, or fluoride, probably owing to their slight solubility, which limits the amount assimilated.[5]

Atomic Weight.—*Approximate Atomic Weight.*—The equivalent of calcium is approximately 20. The most appropriate position for calcium in the Periodic Table indicates a valency of two, and, therefore, an atomic weight of about 40. The specific heat determinations of Eastman and Rodebush give a little over 0·16 for calcium at the ordinary temperature, and assuming, according to Dulong and Petit's Law, an atomic heat of about 6·4, an atomic weight of 40 is again obtained.

Exact Atomic Weight.—Berzelius, in 1809, obtained 7·75 grm. of silver chloride from 3·01 grm. of fused calcium chloride, giving 40·44 [6] as the atomic weight of calcium. In 1841 Baup [7] analysed a series of organic salts of calcium, and obtained a mean value of 249·845 (O=100), or 39·98 (O=16). Dumas [8] calcined very pure Iceland spar, and compared the ratio calcium carbonate to calcium oxide, obtaining as percentage of oxide 56·12, 56·04, and 56·06, which gave a mean value of 40·17 as the atomic weight of calcium. The same method was adopted by Erdmann and Marchand in their first publication.[9] A precipitated carbonate was also calcined, and the value 40·0 obtained. At the same time pure Iceland spar was transformed into sulphate, and from the change in weight gave 40·021 as the atomic weight.

Most of the later investigators adopted modifications of these processes, and their results are summarised on the following page [6] :—

The work on which depends the value at present accepted for the atomic weight of calcium is that of Richards and Hönigschmid. As early as 1899 Richards communicated to the American Association for the Advancement of Science his first experiments in this direction, and published the work in 1902.[10] He obtained anhydrous calcium chloride by fusing in a current of dry hydrochloric acid, dissolved it in water, and weighed the chlorine as silver chloride. The mean value of the ratio $2AgCl : CaCl_2$ from five experiments was 100 : 38·7195, giving an atomic weight of 40·084.

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[1] A condition characteristic of the disease popularly known as " rickets."
[2] Aron and Sebauer, *Biochem. Zeitsch.*, 1908, 8, 1.
[3] Lyman, *J. Biol. Chem.*, 1917, 30, 1.
[4] Shedd, *Soil Science*, 1920, 10, 1.
[5] Coupin, *Compt. rend.*, 1900, 130, 791.
[6] All atomic weights in this section have been recalculated from the experimental data given in the original memoirs, using the following atomic weight values :—

<table>
<tr><td>O = 16·000</td><td>Br = 79·916</td><td>S = 32·065</td></tr>
<tr><td>Cl = 35·457</td><td>Ag = 107·880</td><td>C = 12·003.</td></tr>
</table>

[7] Baup, *Annalen*, 1844, 52, 212.
[8] Dumas, *Compt. rend.*, 1842, 14, 537.
[9] Erdmann and Marchand, *J. prakt. Chem.*, 1842, 26, 461 ; *Annalen*, 1842, 44, 216.
[10] Richards, *Zeitsch. anorg. Chem.*, 1902, 31, 271 ; *J. Amer. Chem. Soc.*, 1902, 24, 374.

Date.	Experimenter.	No. of Experiments	Ratio Measured.	Atomic Weight
1843	Berzelius [1] . .	5	$CaSO_4 : CaO$ 100 : 41·246	40 22
1844	Erdmann and Marchand [2]	6	$CaCO_3 : CaO$ 100 : 56 028	40 07
1850	Erdmann and Marchand [3]	..	$CaCO_3 : CaO$ 100 : 55 991	39·98
1859	Dumas [4] . .	5	$CaCl_2 : 2Ag$ 100 : 194·527	39 98
1897	Herzfeld [5] . .	3	$CaCO_3 : CaO$ 100 : 55 983	39 965
1901	Hinrichsen [6] .	4	$CaCO_3 : CaO$ 100 : 56·062	40 145
1902	Hinrichsen [7] .	2	$CaCO_3 : CaO$ 100 : 56 060	40 140

In 1910 and 1911 Richards and Hönigschmid [8] published the results of experiments carried out with precautions calculated to ensure a very high degree of accuracy. The original papers should be read. The ratios measured were: calcium bromide to the silver required to precipitate it, determined by titration with silver nitrate; calcium bromide to the weight of silver bromide obtained from it; and calcium chloride to the silver required to precipitate it. The salts were prepared by the action of hydrobromic or hydrochloric acid on calcium carbonate. The purest initial materials were employed. The final stages in the purification of the products were conducted in platinum or quartz vessels, and during the operations of transference and evaporation the substances were very carefully protected from all dust or contaminating vapours.

Six measurements of the ratio $CaBr_2 : 2Ag$ gave a mean value of 92·6502 : 100, and hence the atomic weight of calcium is $40·0701 \pm 0·0007$. Six determinations of the ratio $CaBr_2 : 2AgBr$ gave a mean value 53·22323 : 100, the atomic weight is therefore 40·0699.[9]

The authors suggested 40·07 (Ag=107·880) as a minimum value for the atomic weight of calcium owing to the instability of calcium bromide and the tendency to form a basic salt. The greater stability

[1] Berzelius, *Annalen*, 1843, 46, 241.

[2] Erdmann and Marchand, *Annalen*, 1844, 52, 210; *J. prakt. Chem.*, 1844, 31, 269.

[3] Erdmann and Marchand, *J. prakt. Chem.*, 1850, 50, 237; *Annalen*, 1850, 76, 219. Correction of previous experiments was made for small loss of carbon dioxide by calcium carbonate, and small retention of carbon dioxide by calcium oxide.

[4] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 190.

[5] Herzfeld, *Ber.*, 1901, 34, 559

[6] Hinrichsen, *Zeitsch. physikal. Chem.*, 1901, 39, 309.

[7] Hinrichsen *ibid.*, 1902, 40, 746.

[8] Richards and Hönigschmid, *J. Amer. Chem. Soc.*, 1910, 32, 1577; 1911, 33, 28.

[9] All atomic weights in this section have been recalculated from the experimental data given in the original memoirs, using the following atomic weight values :-

O = 16·000   Br = 79·916   S = 32·065
Cl = 35·457   Ag = 107·880   C = 12·003.

of the chloride was the reason for the selection of the third ratio $CaCl_2 : 2Ag$. Seven experiments gave a mean value $= 51 \cdot 44054 : 100$, resulting in an atomic weight $40 \cdot 077$, and probable error $0 \cdot 0004$.[1] They suggested $40 \cdot 075$ as the most reliable value. The International Commission on Atomic Weights for 1925, however, have adopted the value

$$Ca = 40 \cdot 07.$$

It is probable that two isotopes of calcium exist of atomic weights 40 and 44 respectively.[2]

Uses.—No very extensive use has hitherto been made of metallic calcium. Its great reactivity has suggested the possibility of its employment in the refining of metals ;[3] for example, the deoxidation of iron.[4] Watts found, however, that phosphorus still remained in the iron after treatment. The replacement of aluminium by calcium in Goldschmidt's thermite reaction has been proposed.[5]

It has been suggested that calcium might be employed as an absorbent in gas analysis,[6] or in the production of high vacua for physical research,[7] since practically all gases, both elementary and compound, may be absorbed by it, either directly or with decomposition.

Calcium has a certain value in the laboratory as a reducing agent. The chief objection to its use in the reduction of oxides and sulphides is the great violence of the reaction and the infusibility of the oxide.[8] The violence may be reduced by the use of the hydride instead of the metal.[9] Silicates are reduced to silicides by calcium.[10]

In organic chemistry calcium may replace sodium, sometimes with advantage, as a reducing[11] or condensing[12] agent. It may also be substituted for magnesium in Grignard's reaction.[13]

ALLOYS OF CALCIUM.

The alloys of calcium have not thus far proved to be of any great commercial importance, but, in common with the pure metal, they may prove to be useful as deoxidisers.[14]

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[1] All atomic weights in this section have been recalculated from the experimental data given in the original memoirs, using the following atomic weight values :—

$O = 16 \cdot 000$	$Br = 79 \cdot 916$	$S = 32 \cdot 065$
$Cl = 35 \cdot 457$	$Ag = 107 \cdot 880$	$C = 12 \cdot 003$.

[2] Aston, *Proc. Phys. Soc.*, 1922, **35**, 197 ; Dempster, *Phys. Review*, 1922, **20**, 631.
[3] Brandenburg and Wiens, D P., Bitterfeld, 187414, [B], 41361 : see *Zeitsch. Elektrochem.*, 1907, **13**, 351 : Austrian Patent, [A], 5962, see *Zeitsch. Elektrochem.*, 1907, **13**, 746.
[4] Watts, *J. Amer. Chem. Soc.*, 1906, **28**, 1152
[5] Beckmann, Beck, and Schlegel, *Ber*, 1905, **38**, 904.
[6] Sieverts, see Chemical Properties, p. 15.
[7] Soddy, *Proc. Roy. Soc.*, 1906, [A], **78**, 429.
[8] Perkin, *Trans. Faraday Soc.*, 1907, **3**, 115.
[9] Perkin and Pratt, *ibid.*, 1908, **3**, 179.
[10] Wedekind and Durr, *Zeitsch. angew. Chem.*, 1912, **25**, [1], 1265.
[11] Beckmann, Beck, and Schlegel, *loc. cit.* ; Neuberg and Marx, *Zeitsch. Ver. deut. Zuckerind.*, 1907, **615**, 456 ; Spencer and Price, *Trans. Chem. Soc.*, 1910, **97**, 385 ;- Marschalk, *Ber.*, 1910, **43**, 641 ; Marshall and Nicolajewsky, *ibid.*, p. 1700 ; Breteau, *Bull. Soc. chim.*, 1911, [4], **9**, 585.
[12] Perkin and Pratt, *Proc. Chem. Soc.*, 1907, **23**, 304 ; 1909, **25**, 18 ; *Trans. Chem. Soc.*, 1909, **95**, 159.
[13] Beckmann, Beck, and Schlegel, *loc. cit.*
[14] Vickers, *Metals and Their Alloys* (Crosby Lockwood & Son), 1923, p. 46.

Cooper [1] has patented an alloy of calcium and aluminium, containing not more than 8 per cent. calcium, for use in casting. The alloy is ductile and specifically lighter than aluminium, and, on account of its lightness, might also be used as a filling for hollow steel structures.[2]

An alloy of calcium and lead, which has received the name of " Ulco " metal, has been put forward as a substitute for antimonial lead in the manufacture of shrapnel bullets.[3] It contains considerably less than 1 per cent. calcium, or, better still, a mixture of calcium and barium. It is much harder than other commercial lead alloys, and it expands on solidification, forming castings free from blow-holes. The Brinell hardness of antimonial lead is about 17, and that of " Ulco " metal 22–26, according to the temperature of pouring. It can be re-melted several times without appreciable loss of hardness, and has the general appearance of ordinary lead. Tests made by the United States Bureau of Standards show that it compares very favourably with Babbitt metal for use in machinery bearings.

A bearing metal containing calcium, with a Brinell hardness of 35–45 and melting-point 370° C., has also been described.[4] It has a yield-point $2\frac{1}{2}$ times as high as that of the corresponding tin alloy. It consists apparently of hard crystals of a calcium-lead compound embedded in a softer mass of mixed crystals of lead and other metals.

A large number of other alloys of calcium have been studied, but they are of theoretical interest only. The general methods of preparation are : (a) simple fusion together of the two metals ; (b) reduction of a calcium salt in the presence of another metal, or simultaneous reduction of a mixture of compounds of the two metals ; (c) electrolysis of the fused calcium chloride, using a cathode of the second metal in the molten state.

The energy with which calcium reacts with the metals increases with increasing atomic weight of the latter.

In general, the alloys decompose water with more or less vigour according to the amount of calcium they contain.

Brief data of the calcium alloys and references to the original pape dealing with them are given in the following table :—

Element alloying with Calcium.	Remarks.	Authority.
Aluminium .	Probably one compound, CaAl₃, m.-pt. 692° C. More than 10 per cent. Ca makes alloys brittle.	Wöhler, *Annalen*, 1866, **138**, 253 ; Arndt, *Ber.*, 1905, **38**, 1972 ; Stockem, *Métallurgie*, 1906, **3**, 147 : Donski, *Zeitsch. anorg. Chem.*, 1908, **57**, 185.
Antimony .	Forms brittle alloys. See p. 101.	Donski, *loc. cit.* ; Setlik, *Chem. Zeit.*, 1905, **29**, 218.

[1] Cooper, U.S.A. Patent, 1224362 (1917).
[2] Brace, *J. Inst. Metals*, 1921, **25**, 153.
[3] Frary and Temple, *Chem. Met. Eng.*, 1918, **19**, 523 ; see *J. Soc. Chem. Ind.*, 1918, **37**, 737A, and *Ann. Rep. Soc. Chem. Ind.*, 1919, **4**, 248 ; Cowan, Simpkins, and Hiers, *Trans. Amer. Electrochem. Soc.*, 1921, **40**, 27. See also Czochralski, *Zeitsch. Metallkunde*, 1920, **12**, 371 ; *Chem. Abs.*, 1921, **15**, 662.
[4] Hart, *Chem. Abs.*, 1920, **14**, 3628 ; see also Rolfe, *J. Inst. Metals*, 1921, **25**, 171.

Element alloying with Calcium.	Remarks.	Authority.
Bismuth	No definite compound.	Donski, *loc. cit.*
Cadmium	Compounds, $CaCd_3$, m.-pt. 615° C. ; α-CaCd, changing to β-CaCd at 635° C., m.-pt. 685° C. : and possibly Ca_3Cd_2, m.-pt. 510° C. with decomposition.	Donski, *loc. cit.*
Copper	Alloy containing 20 per cent. Ca is pure white and crumbles on exposure to air. Compound Cu_4Ca, m.-pt. 935° C., and possibly $CuCa_4$, m.-pt. 480° C.	Stockem, *Métallurgie*, 1906, **3**, 147 ; Hackspill, *Compt. rend.*, 1906, **142**, 89 ; Baar, *Zeitsch. anorg. Chem.*, 1911, **70**, 352.
Iron	Doubt as to whether alloy is formed or not. Pressure is apparently necessary.	Watts, *J. Amer. Chem. Soc.*, 1906, **28**, 1152 ; Quasebart, *Métallurgie*, 1906, **3**, 28 ; Stockem, *loc. cit.* ; Hirsch and Aston, *Trans. Amer. Electrochem. Soc.*, 1908, **13**, 143.
Lead	Compounds, Pb_3Ca_2, m.-pt. 775° C., density at 19° C. 7 6 ; Pb_3Ca, m.-pt. 649° C. ; PbCa, m.-pt. 949° C. with decomposition ; $PbCa_2$, m.pt. 1112° C.	Caron, *Compt. rend.*, 1859, **48**, 440 ; Moissan, *Ann. Chim. Phys.*, 1899, **18**, 295 ; Pring, *Trans. Chem. Soc.*, 1905, **87**, 1530 ; Hackspill, *Compt. rend.*, 1906, **143**, 227 ; Donski, *loc. cit.* ; Baar, *loc. cit.* ; Moldenhauer and Andersen, *Zeitsch. Elektrochem.*, 1913, **19**, 444.
Magnesium	Brittle alloy. Compound Mg_4Ca_3, m.-pt. 715° C., stable in air. Density at 25° C. 1·701, and heat of formation 43 Cal.	Moissan, *loc. cit.* ; Stockem, *loc. cit.* ; Baar, *loc. cit.* ; Biltz and Hohorst, *Zeitsch. anorg. Chem.*, 1921, **121**, 1.
Mercury	Several solid crystalline compounds described, Ca_3Hg_4, $CaHg_2$, $CaHg_4$, m.-pt. 266° C. ; $CaHg_5$, $CaHg_8$, and $CaHg_9$.	Moissan and Chavanne, *Compt. rend.*, 1905, **140**, 122 ; Férée, *Compt. rend.*, 1898, **127**, 618 ; Schürger, *Zeitsch. anorg. Chem.*, 1900, **25**, 425 ; Cambi and Speroni, *Atti. R. Accad. Lincei*, 1914, [5], **23**, ii., 599 ; Cambi, *ibid.*, p. 606 ; Smith, *J. Amer. Chem.*

Element alloying with Calcium.	Remarks.	Authority.
Mercury (*continued*)		*Soc.*, 1915, **37**, 76. See also Neuhausen, *J. Amer. Chem. Soc.*, 1922, **44**, 1445; Guertler, *Metallographic*. vol. ii., Pt. I., iii. (Gebrüder Borntraeger), 1921, p. 237.
Nickel .	Brittle alloy.	Moissan, *loc. cit.*
Silver .	Even small quantities of Ca make the alloy grey and brittle. Brittleness increases up to 86 per cent. Ca and then decreases. Compounds, Ag_3Ca, m.-pt. 725° C. ; $AgCa$, m.-pt. 670° C. ; $AgCa_2$, m.-pt. 555° C. ; Ag_4Ca, m.-pt. with decomposition, 683° C. ; Ag_2Ca, m.-pt. with decomposition, 595° C.	Hackspill, *Compt. rend.*, 1906, **142**, 89 ; Baar, *loc. cit.*
Sodium .	Miscible to limited extent in liquid state but separate on cooling.	Moissan, *Compt. rend.*, 1898, **126**, 1753 ; Muthmann, Weiss, and Metzger, *Annalen*, 1907, **355**, 137.
Thallium .	Compounds, Tl_3Ca, decomposition at 524° C.; Tl_4Ca_3, m.-pt. with decomposition at 555° C.; $TlCa$, m.-pt. 969° C.	Donski, *loc. cit.*
Tin . .	$CaSn_3$, m.-pt. 624° C.	Moissan, *Ann. Chim. Phys.*, 1899, [7], **18**, 289.
Zinc . .	$CaZn_{10}$, m.-pt. 717° C., heat of formation 199·1 ±4·7 Cal. and heat of fusion 77 cal. per grm.; $CaZn_4$, m.-pt. 680° C. with decomposition, heat of formation 55·6 ±3 Cal. ; Ca_2Zn_3, m.-pt. 688° C. ; Ca_4Zn, m.-pt. 385° C. with decomposition. Alloys containing 0–6 per cent. Ca are a little harder than zinc. Brittleness increases up to 30 per cent. Ca.	Moissan, *loc. cit.* ; Donski, *loc. cit.* ; Moldenhauer and Andersen, *Zeitsch. Elektrochem.*, 1913, **19**, 144; Roos, *Zeitsch. anorg. Chem.*, 1916, **94**, 329.

See also Giua and Giua-Lollini, *Chemical Combination among Metals,* translated by G. W. Robinson (Churchill), 1918.

COMPOUNDS OF CALCIUM.

General Properties of Compounds of Calcium.—With certain minor exceptions, calcium behaves as a divalent element. The calcium ion is colourless, so that a coloured salt is, in general, only obtained with a coloured anion ; for example, calcium chromate is yellow. There is a decided tendency to form double salts, especially with the salts of the alkali metals.

CALCIUM AND HYDROGEN.

Calcium Hydride, CaH_2.—By heating lime with magnesium in an atmosphere of hydrogen, Winkler obtained an earthy substance which he regarded as a mixture of magnesium oxide with calcium hydride, to which he gave the formula CaH.[1] Probably unattacked calcium still remained. Calcium hydride, CaH_2, is formed by the direct combination of calcium with hydrogen, the rate of reaction depending on the physical state of the metal as well as on the temperature.[2] The most favourable temperatures, apparently, are between 150° C. and 300° C., and above 600° C. A superficial layer of hydride facilitates further absorption.[2]

It may also be prepared by fusing lime electrically in a current of hydrogen and cooling the product in hydrogen.[3]

Calcium hydride is a white crystalline body of density 1·7, insoluble in the usual solvents, and capable of being heated up to 600° C. *in vacuo* without decomposition.[1] It does not conduct electricity, indicating that it is not to be regarded as an alloy,[5] since hydrogen does not function as a metal.[6]

Calcium hydride is more stable than either strontium or barium hydrides.[7]

Recent observations seem to show that calcium hydride and calcium form a complete series of solid solutions, and also that calcium will dissolve hydrogen without combining with it. The latter fact probably explains Sieverts' observations, to which reference has already been made. The absorption of hydrogen at low temperatures is no doubt due to simple solution which ceases at 300° C., whilst hydride formation does not begin until 600° C. is reached.[7]

These different solution phenomena make it difficult to determine the dissociation pressure of the hydride because the system is divariant. At 810° C. the dissociation pressure of the pure hydride is 290 mm., but it is lowered by the presence of the metal up to a concentration of 48 milligram-molecules of calcium per gram of hydride. It is, therefore, evident that hydride formation may take place at a temperature much higher than the dissociation temperature of the pure hydride.[7]

[1] Winkler, *Ber.,* 1891, 24, 1974; see also von Lengyel, *Chem. Zentr.,* 1898, 69, ii., 262.
[2] Sieverts, *Chem. Zeit.,* 1915, 39, 804. See Ephraim and Michel, *Helv. Chim. Acta,* 1921, 4, 900 ; Bardwell, *J. Amer. Chem. Soc.,* 1922, 44, 2499.
[3] Kiesewalter, German Patent, 311987 ; see *J. Soc. Chem. Ind.,* 1920, 39, 406A.
[4] Moissan, *Compt. rend.,* 1898, 127, 29 ; *Ann. Chim. Phys.,* 1899, [7], 18, 289.
[5] Moissan, *Ann. Chim. Phys.,* 1905, [8], 6, 289.
[6] See this series, Vol. II.
[7] Ephraim and Michel, *loc. cit.*

From his study of the dissociation pressures of the hydride between 641° C. and 747° C., Brønsted calculated the heat of formation at 18° C. to be 43·930 Cal. as against the observed value 45·100 Cal.[1]

It is a valuable reducing agent, especially for organic substances,[2] and can be kept more under control than metallic calcium.[3] Methane may be synthesised by the action of carbon, carbon monoxide, or carbon dioxide, on calcium hydride.[4]

At 100° C. calcium hydride. in common with the other alkaline earth hydrides, reacts with acetylene, producing an acetylenic acetylide. $CaC_2.C_2H_2$, and liberating hydrogen. If this compound be warmed gently *in vacuo* the carbide may be obtained at a low temperature.[5]

Calcium hydride under the name of " hydrolith," as a portable form of hydrogen, has been made the subject of patents issued by Jaubert.[6] It contains 90 per cent. pure calcium hydride mixed with some oxide and nitride. When acted upon by water, 1 kgm. produces 1 cub. metre of hydrogen. It has been employed in the French army for the filling of dirigibles. " Hydrogenite " is a mixture similar in its behaviour to " thermite," and contains the hydride, a certain amount of a metal or alloy, and water in the form of a hydrated body such as slaked lime. When heated at one point reaction proceeds vigorously throughout the mass and yields hydrogen.[7]

When a solution of calcium hydride in a fused eutectic mixture of potassium and lithium chloride is electrolysed, the hydrogen behaves as a halogen and is liberated at the anode in the proportion required by Faraday's law.[8]

Other Hydrides.—From vapour-pressure measurements Moldenhauer and Roll-Hansen[9] concluded that a lower hydride of calcium, CaH, exists, but their results were probably due to inequalities of temperature in the tube in which the hydride was heated.[10]

Hoffmeister supposed that he had discovered a gaseous hydride of calcium, but this result has received no further confirmation.[11]

CALCIUM AND FLUORINE.

Calcium Subfluoride, CaF or Ca_2F_2.—Guntz and Bassett[12] attempted to prepare a subchloride, subiodide, and subfluoride by heating together mixtures of metallic calcium with the chloride, iodide, and fluoride respectively, under varying conditions. They came to the[1]

[1] Brønsted, *Zeitsch. Elektrochem.*, 1914, **20**, 81 ; see also Gautier, *Compt. rend.*, 1902, **134**, 1108 ; Guntz and Bassett found 46·200 Cal., *Compt. rend.*, 1905, **140**, 863.
[2] Reich and Serpek, *Helv. Chim Acta*, 1920, **3**, 138. See also Ebler and Bender, *Zeitsch. anorg. Chem.*, 1913, **83**, 149 ; Ebler and Herrdigen, *Ber.*, 1913, **46**, 2264.
[3] Perkin, *Trans. Faraday Soc*, 1907, **3**, 115 ; Perkin and Pratt, *ibid.*, 1908, **3**, 179.
[4] Mayer and Altmayer, *Ber.*, 1908, **41**, 3074.
[5] Moissan, *Compt. rend.*, 1903, **136**, 1524.
[6] Jaubert, *Compt. rend.*, 1906, **142**, 788 ; French Patent, 327878 (1902) ; English Patent, 25215 (1907) ; see also Krull, *Zeitsch. angew. Chem.*, 1906, **19**, 1233 ; Tomkinson, *Chem. News*, 1921, **122**, 241.
[7] Jaubert, English Patents, 153, 9623 (1911) ; 5005 (1912) ; French Patents, 427191 (1910) ; 438021 (1911) ; U.S.A. Patent, 1099446 (1914).
[8] Bardwell, *J. Amer. Chem. Soc.*, 1922, **44**, 2499.
[9] Moldenhauer and Roll-Hansen, *Zeitsch. anorg. Chem.*, 1913, **82**, 130.
[10] Marino, *Atti R. Accad. Lincei*, 1915, [5], **24**, ii., 143.
[11] Hoffmeister, *Zeitsch. anorg. Chem.*, 1906, **48**, 137.
[12] Guntz and Bassett, *Bull. Soc. chim.*, 1906, [3], **35**, 404.

conclusion, however, that the so-called subhalides were merely mixtures of unaltered salt with a little hydride and oxide, resulting from the accidental presence of small quantities of water. Hence the property of liberating hydrogen from water, shown by these products, was due to the action of hydride on water.

Wöhler and Rodewald,[1] on the other hand, stated that by heating together calcium and calcium fluoride above 1400° C. in a steel tube, protected by wrapping in platinum foil and coating with basic fireclay, crystals were obtained of a red to orange-yellow colour with a metallic lustre, and of composition corresponding to the formula CaF. Formation only began above 1100° C. Below this temperature the compound split up into metallic calcium and the fluoride. To obtain the subfluoride stable at the ordinary temperature, it had to be cooled rapidly by quenching in solid carbon dioxide. By treatment with bromoform the subfluoride could be separated from the fluoride owing to difference of density. The subfluoride is not so deliquescent as the subchloride and subiodide, and is less easily attacked. The density at 20° C. is 2·305.

Calcium Fluoride, CaF_2.—The best-known natural form of calcium fluoride is the mineral fluorite or fluorspar, crystallising in the cubic system. It is often richly coloured, for example, blue fluorite, or Blue John, from the famous Blue John mines near Castleton, in Derbyshire, and a red fluorite found near Ashover in the same county.[2] The colour is not homogeneously distributed, but appears to form films at the crystal surfaces, especially at the junctions. The colour of Blue John is probably of organic origin,[3] but that of red fluorite is due to small quantities of limonite, $Fe_4O_3(OH)_6$.[2] Other coloured varieties are also known, and in fluorspar districts the carving of ornamental vases from the mineral often forms an important industry. When gently warmed, the mineral fluoresces, and this circumstance gave rise to the term fluorescence.

The fluoride also occurs associated with the phosphate as fluorapatite, and is found in small quantities in teeth and bones.

It may be formed by direct union of its elements (see page 15). The heat of formation is 239·18 Cal.[4] By neutralising calcium hydroxide or carbonate [5] with hydrofluoric acid, it is obtained as a white precipitate, crystalline in the case of the carbonate. The heat of neutralisation $Ca(OH)_2Aq+HF$ is 18·155 Cal.[6] Addition of a calcium salt to a solution of a neutral fluoride gives a gelatinous precipitate, but boiling the latter with very dilute hydrochloric acid transforms it into the crystalline variety.[7]

A crystalline compound may also be prepared if a mixture of ten parts of calcium chloride and one of manganese fluoride is fused in an atmosphere of carbon dioxide at 800°–1400° C. On treating the product with water, and then dilute hydrochloric acid, calcium fluoride is obtained as octahedral crystals if the fusion has taken place under

[1] Wöhler and Rodewald, *Zeitsch. anorg. Chem.*, 1909, **61**, 54.
[2] Garnett, *Trans. Chem. Soc.*, 1920, **117**, 620.
[3] Blount and Sequeira, *Trans. Chem. Soc.*, 1919, **115**, 705 ; Sakao and Hirose, *Mem. Coll. Sci. Kyōtō*, 1921, 4, 349 ; see *Trans. Chem. Soc.*, 1922, **122**, Abs. ii., 779.
[4] de Forcrand, *Ann. Chim. Phys.*, 1911, [8], **24**, 256. Guntz and Bassett gave the value 237·4 Cal., *Compt. rend.*, 1905, **140**, 863.
[5] Berzelius, *Pogg. Annalen*, 1824, **1**, 20.
[6] Petersen, *Zeitsch. physikal. Chem.*, 1889, **4**, 384.
[7] Moissan, *Bull. Soc. chim.*, 1891, [3], **5**, 152.

1000° C., or cubes if over 1200° C.[1]   Potassium hydrogen fluoride may be used instead of manganese fluoride.[2]

By pouring potassium fluoride solution into an excess of calcium chloride solution a colloidal solution of calcium fluoride can be prepared.[3] By dialysis, succeeded by concentration over sulphuric acid *in vacuo*, a 2 per cent. solution can be obtained.   The colloid shows the charge of the ion in excess at the time of precipitation, in accordance with Lottermoser's observation.[4]

A plastic form of calcium fluoride has also been described.[5]

The melting-point of fluorspar is 1378° C.,[6] the density 3·16,[7] and the specific heat 0·21492.[8]   Fluorspar is very transparent to ultra-violet rays, the shortest wave-length penetrating it being probably 1230 Å.[9]

According to Frémy,[10] calcium fluoride is decomposed by water and by oxygen at red heat, producing hydrofluoric acid and probably fluorine respectively.   Chlorine also decomposes it, an equilibrium point being reached.

The solubility of the natural fluorspar, determined by measurement of the electrical conductivity of the saturated solution,[11] is 15·07 mgm. per litre at 18° C., and that of the precipitated fluoride, 16·3 mgm. per litre.   The solubility increases with rise in temperature, and the heat of solution is −2·7 Cal.[12]   Concentrated acids increase the solubility of the salt considerably, and on heating with concentrated sulphuric acid, hydrofluoric acid is obtained, this being, in fact, the commercial process for the production of the latter.   Hydrofluoric acid itself also increases the solubility, probably through the formation of a complex ion.   The salt $CaF_2.2HF.6H_2O$ has been obtained in the solid state.[13]

Fluorite is used for optical purposes.[14]

In the soil calcium has a beneficial effect on plants.[15]

Fluorspar is used as a flux in various metallurgical operations; in fact, its employment for this purpose dates from very early times and is the origin of its name.

CALCIUM AND CHLORINE.

Calcium Subchloride, CaCl or Ca_2Cl_2.[16]—In carrying out experiments on the preparation of calcium by electrolysis of the fused chloride,

[1] Defacqz, *Compt. rend.*, 1903, **137**, 1251.

[2] Poulenc, *Ann. Chim. Phys.*, 1894, [7], **2**, 24.

[3] Paternò and Mazzuchelli, *Atti R. Accad. Lincei*, 1903, [5], **12**, ii., 420, 520; Mazzuchelli and Vita, *Gazzetta*, 1920, **50**, i., 232.

[4] Lottermoser, *J. prakt. Chem.*, 1905, **72**, 39.

[5] Cohn, *Zeitsch. angew. Chem.*, 1911, **24**, 1209.

[6] Karandéeff, *Zeitsch. anorg. Chem.*, 1910, **88**, 188.   Ruff and Plato found 1330° C. *Ber.*, 1903, **36**, 2357.

[7] Ruff and Plato, *Ber.*, 1902, **35**, 3612; see also Schiff, *Annalen*, 1858, **108**, 23.

[8] Regnault, *Ann. Chim. Phys.*, 1841, [3], **1**, 129; Kopp found 0·209, *Annalen Suppl.* 1864–5, **3**, 293.

[9] Martens, *Ann. Physik.*, 1901, [4], **6**, 603.

[10] Frémy, *Ann. Chim. Phys.*, 1856, [3], **47**, 5.

[11] Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, **64**, 129.

[12] de Forcrand, *loc. cit.*

[13] Frémy, *loc. cit.*

[14] Gifford, *Proc. Roy. Soc.*, 1902, **70**, 329.

[15] Ampola, *Gazzetta*, 1904, **34**, ii., 156; Keijiro Aso, *Bull. Coll. Agr. Tokyo Imp. Univ.*, 1906, **7**, 85; see *J. Chem. Soc.*, 1906, **90**, Abs. ii., 888; Gautier and Clausmann, *Compt. rend.*, 1919, **169**, 115.

[16] See Calcium Subfluoride, p. 24.

a product regarded as a subchloride, Ca_2Cl_2, has sometimes been obtained.[1] Wöhler and Rodewald[2] obtained the subchloride by a method similar to that which they employed for the subfluoride. Calcium and calcium chloride in equivalent proportions were heated together for 24 hours, at 900°–1000° C., in steel cylinders of 9 c.c. capacity. This was followed by rapid quenching in solid carbon dioxide. The metallic calcium was removed by floating off in ethyl iodide, and bromoform was used to separate the subchloride from the chloride. Red-violet crystals, which recalled Borchers and Stockem's product, were obtained. The temperature which must be reached before the formation of subchloride can take place, was found to be about 800° C. This explains why, in the electrolysis of calcium chloride, the production of the subchloride can be avoided by keeping the temperature below 800° C.

When calcium subchloride is acted upon by water it gives calcium chloride, calcium hydroxide, and hydrogen.

$$Ca_2Cl_2 + 2H_2O = CaCl_2 + Ca(OH)_2 + H_2.$$
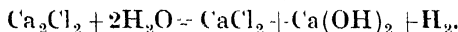
Calcium Chloride, $CaCl_2$.—Calcium chloride occurs in nature as the mineral tachydrite, a double chloride of magnesium and calcium, $CaCl_2,2MgCl_2,12H_2O$. It is also present in sea-water. The part played by tachydrite in the formation of oceanic salt deposits has been studied by van 't Hoff and his colleagues.[3]

Calcium chloride may be obtained by direct combination of its elements. The reaction does not take place in the cold, but is very vigorous on the application of heat.[4] The heat of formation is 190·44 Cal.[5]

It can be prepared by neutralisation of calcium carbonate or oxide with hydrochloric acid and evaporation to dryness. To obtain the anhydrous salt the residue must be fused, but as the action of water vapour tends to decompose it and make it alkaline, hydrochloric acid gas followed by nitrogen must be passed over it.[6]

Anhydrous calcium chloride is a white solid of density 2·15 at 20° C.[7] The density in the molten state has also been determined.[8] The following values at different temperatures have been found :—

Temperature, ° C.	Density.
800	2 048
850	2 026
900	2 002

[1] Borchers and Stockem, *Zeitsch. Elektrochem.*, 1902, 8, 757 ; *Ber.*, 1903, 36, 17 ; Daneel and Stockem, *Zeitsch. Elektrochem*, 1905, 11, 209 ; but see Johnson. *Trans. Amer. Electrochem. Soc*, 1910, 18, 143.

[2] Wöhler and Rodewald, *Zeitsch. anorg. Chem.*, 1909, 61, 54.

[3] van 't Hoff and d'Ans, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 913 ; van 't Hoff, Kenrick, and Dawson, *Zeitsch. physikal. Chem.*, 1902, 39, 27.

[4] Moissan, *Ann. Chim Phys*, 1899, [7], 18, 289.

[5] de Forcrand, *Ann. Chim. Phys.*, 1911, [8], 24, 256. Guntz and Bassett gave the value 190·3, *Compt. rend.*, 1905, 140, 863.

[6] Richards and Hönigschmid, *J. Amer. Chem. Soc.*, 1911, 33, 28.

[7] Richards and Hönigschmid, *loc. cit.*

[8] Arndt and Loewenstein, *Zeitsch. Elektrochem.*, 1909, 15, 784.

The more recent determinations of the melting-point give values lying between 770° and 780° C.

Melting-point, ° C.	Authority.
780	Ruff and Plato, *Ber.*, 1903, **36**, 2367.
774	Arndt, *Zeitsch. Elektrochem.*, 1906, **12**, 337.
773 9	Plato, *Zeitsch. physikal. Chem.*, 1907, **58**, 350.
772	Karandéeff, *Zeitsch. anorg. Chem.*, 1910, **68**, 188.
777	Menge, *Zeitsch. anorg. Chem.*, 1911, **72**, 162.
773	Schaefer, *Jahrb. Miner.*, 1919, Beil. Bd., **43**, 132.

The specific heat.[1] between 23° and 99° C. is 0·16420.

Values for the electrical conductivity of fused calcium chloride at different temperatures are given in the following table [2] :—

Temperature, ° C.	Specific Conductivity.	Equivalent Conductivity.
800	2·10	56 9
850	2 27	62 3
900	2 40	66 6
950	2 51	70·4

Arndt and Willner [3] found the decomposition potential at 800° C. to be 3·24 volts. According to Neumann and Bergve [4] it is 2·85 volts at 585° C.,[5] and the temperature coefficient is $0·685 \times 10^{-3}$. The actual working voltage in the separation of the metal is very much higher.

The fused salt becomes phosphorescent on exposure to sunlight, and really constitutes Homberg's phosphorus.

Calcium chloride is very deliquescent, which makes it a valuable drying agent in the laboratory and in technology.[6] According to McPherson,[7] the porous granular calcium chloride, obtained by drying a little above 260° C., is a more rapid and more efficient desiccating agent than the fused salt, because the action is due to absorption rather than to hydration, and the porous form naturally exposes more surface. At 25° C. the vapour pressure of the fused salt is 0·35 mm. and of the granular 0·14–0·25 mm.

The solution of anhydrous calcium chloride in water is accompanied by considerable heat evolution. The molecular heat of solution is 17·48 Cal.[8]

Berthelot and Ilosvay stated that the heat of solution of recently fused salt is about 0·300 Cal. greater than that of the same salt two

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[1] Regnault, *Ann. Chim. Phys.*, 1841, [3], **1**, 129.

[2] Arndt and Loewenstein, *loc. cit.*

[3] Arndt and Willner, *Zeitsch. Elektrochem.*, 1908, **14**, 216.

[4] Neumann and Bergve, *ibid.*, 1915, **21**, 152.

[5] The temperature of fusion was reduced by the addition of lithium chloride and calcium fluoride.

[6] See this series, Vol. IX., Part III.

[7] McPherson, *J. Amer. Chem. Soc.*, 1917, **39**, 1317.

[8] de Forcrand, *Compt. rend.*, 1911, **152**, 27 ; see also Pickering, *Ber.*, 1894, **27**, 67.

months later, apparently indicating the presence of another modification.[1] An observation made by Richards and Hönigschmid[2] supports this conclusion. In the last stages of the preparation of pure calcium chloride for their atomic weight determinations, they heated it first in a current of gaseous hydrochloric acid and then replaced this by nitrogen. When the product was cooled, a clear glassy solid was at first formed, but this soon became flecked with white spots which increased until they covered the whole surface. They were caused by the shattering of the glassy chloride as it crystallised, sometimes almost explosively,
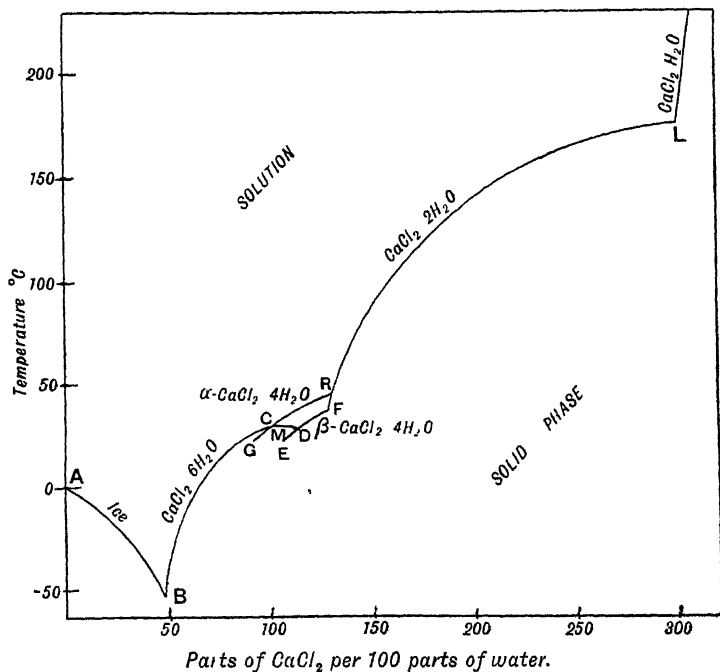
FIG. 1.—Equilibria in the system, calcium chloride: water.

at a lower temperature. The transition could be prevented by heating for a long time in nitrogen. The authors concluded that either traces of hydrochloric acid dissolved in the fused salt hastened crystallisation, or that traces of alkali formed by long ignition in nitrogen retarded it. The change was accompanied by considerable increase in volume, but the density was not determined.

The Hydrates of Calcium Chloride.—Calcium chloride forms four hydrates containing 6, 4, 2, and 1 molecules of water of crystallisation respectively.[3] The behaviour of the system, calcium chloride : water, under varying conditions of temperature and concentration, was first explained by Roozeboom[4] from the point of view of the phase rule.

In fig. 1 the temperatures of saturation with respect to the different

[1] Berthelot and Ilosvay, *Ann. Chim. Phys.*, 1883, [5], 29, 295.
[2] Richards and Hönigschmid, *J. Amer. Chem. Soc.*, 1911, 33, 28.
[3] Müller-Erzbach, *Ber.*, 1886, 19, 127; Lescœur, *Compt. rend.*, 1881, 92, 1158; *Bull. Soc. chim.*, 1881, [2], 36, 2.
[4] Roozeboom, *Zeitsch. physikal. Chem.*, 1889, 4, 31.

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[1] Berthelot and Ilosvay, *Ann. Chim. Phys.*, 1883, [5], **29**, 295.
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[3] Müller-Erzbach, *Ber.*, 1886, **19**, 127 ; Lescœur, *Compt. rend.*, 1881, **92**, 1158 ; *Bull. Soc. chim.*, 1881, [2], **36**, 2.
[4] Roozeboom, *Zeitsch. physikal. Chem.*, 1889, **4**, 31.

Between M and D the liquid is richer in calcium chloride than the solid. D is a second eutectic at which a tetrahydrate begins to separate out, and the curve DF is the solubility or freezing-point curve for this compound. At D the composition of the solution is 112·8 parts of calcium chloride to 100 of water. More or less parallel to DF is a second curve CR, which also represents the solubility curve of a tetrahydrate, so that there must be two modifications of the tetrahydrate, an α- and a β-form. These were first distinguished by Roozeboom. The β-form, separating along DF, is more soluble than the α-compound, and is, therefore, a metastable hydrate. By inoculating a solution, of which the temperature and pressure are given by any point inside the region CRFD, with a minute crystal of α-CaCl₂.4H₂O, the latter will begin to separate out until the temperature and composition of the remaining solution correspond to a point on the curve CR. The melting-point of the hexahydrate is, therefore, in a metastable region, and represents a case of suspended transformation, illustrating the general tendency of a system to pass through an unstable phase before reaching a state of stable equilibrium. Under stable conditions the α-tetrahydrate would begin to separate when the composition had reached 100·6 parts of calcium chloride per 100 parts of water, and when the temperature was still a little under the melting-point of the hexahydrate.

Supersaturation of both the α- and β-tetrahydrate solutions can be obtained. The solubility curve of the α-compound may be extended to point G, where the concentration of the liquid phase is 91 grm. of calcium chloride per 100 grm. of water at 20° C., and the β-curve to E, concentration 104·5 grm. at 20° C. In either case inoculation of the solution with the hexahydrate causes rapid separation of the latter.

At R and F, that is at temperatures 45·3° and 38·4° C., and solubilities 130·2 and 127·5 respectively, the α- and β-tetrahydrates are in equilibrium with the dihydrate of which the solubility curve is represented by FL. At a temperature of 175·5° C., and solubility 297 grm. of calcium chloride per 100 grm. of water, the monohydrate appears, the solubility curve of the anhydrous salt does not begin until a temperature of over 260° C. is reached.

The vapour pressures at the different transition-points are as follows [1] :—

Temp., ° C.	Pressure, mm. Hg.	Composition of Phases.		
		Solid.	Solution.	Vapour.
- 55	0	Ice ; CaCl₂.6H₂O	CaCl₂ : 14·5H₂O	H₂O
+ 29·2	5·67	CaCl₂.6H₂O ; β-CaCl₂.4H₂O	CaCl₂ : 5·41H₂O	,,
+ 29·8	6·80	CaCl₂.6H₂O ; α-CaCl₂.4H₂O	CaCl₂ : 6·10H₂O	,,
+ 38·4	7·88	β-CaCl₂.4H₂O ; CaCl₂.2H₂O	CaCl₂ : 4·83H₂O	,,
+ 45·3	11·77	α-CaCl₂.4H₂O ; CaCl₂.2H₂O	CaCl₂ : 4·73H₂O	,,
+175·5	842	CaCl₂.2H₂O ; CaCl₂.H₂O	CaCl₂ : 2·07H₂O	,,
ar +260	Several atmos.	CaCl₂.H₂O ; CaCl₂	CaCl₂ : near 1·8H₂O	,,

[1] Roozeboom, *Zeitsch. physikal. Chem.*, 1889, **4**, 42.

The solubility of calcium chloride is considerably diminished by the presence of hydrochloric acid,[1] and the transition-points are lowered.[2] Migration experiments in hydrochloric acid solutions indicate the existence of complex anions of the type $(CaCl_2)_xCl'_x$.[3]

The following values have been found for the boiling-points of solutions of different concentrations[4] :—

Grams CaCl₂ in 100 grams water	6	16 5	25	41·5	69 0	101	137·5	178	220	268	292	305
Boiling-point, °C.	101	103	105	110	120	130	140	150	160	170	175	178

The properties of calcium chloride solutions have also been investigated from the point of view of density,[5] freezing-point,[6] vapour pressure,[7] specific heat,[8] viscosity,[9] surface tension,[10] electrical conductivity,[11] compressibility,[12] and refractive index.[13]

Calcium Chloride Hexahydrate, $CaCl_2.6H_2O$, forms hexagonal prisms by crystallisation from the saturated solution at ordinary temperatures.[14] Its density at 22° C. is 1·7182.[15] The heat of formation of the hydrate from the anhydrous salt and water is 21·750 Cal.[16] The heat of solution is −4·596 Cal. at 17·9° C.,[17] or −4·562 Cal. at 22° C.[18] The heat of fusion is 11·417 Cal.[19]

Tammann studied the effect of pressure on the melting-point of the hexahydrate.[20] His results are contained in the table on following page.

Calcium Chloride Tetrahydrate, $CaCl_2.4H_2O$.—Lefèbvre[21] and Hammerl[22] each discovered a tetrahydrate. These were at first considered to be identical, since the solubilities were not determined. Roozeboom distinguished between them. Hammerl's was the α-form,

[1] Engel, *Ann. Chim. Phys.*, 1888, [6], 13, 370.
[2] Milikan, *Zeitsch. physikal. Chem.*, 1917, 92, 496.
[3] Hixon, *J. Chem. Soc.*, 1922, 122, Abs. ii., 815.
[4] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 426 ; see also Emden, *Wied. Annalen*, 1887, [2], 31, 188.
[5] Schiff, *Annalen*, 1859, 110, 71 ; Jones and Getman, *Zeitsch. physikal. Chem.*, 1904, 49, 400.
[6] de Coppet, *Ann. Chim. Phys.*, 1872, [4], 25, 519 ; 26, 110 ; Arrhenius, *Z. physikal. Chem.*, 1888, 2, 491 ; Jones and Getman, *loc. cit* ; *Zeitsch. physikal.*, 1903, 46, 244 ; Jones and Chambers, *Amer Chem. J.*, 1900, 23, 89.
[7] Emden, *Wied. Annalen*, 1887, [2], 31, 170 ; Biltz, *Zeitsch. physikal. Chem.*, 1902, 4
[8] Person, *Ann. Chim. Phys.*, 1851, [3], 33, 437 ; Marignac, *ibid.*, 1876, [5], 8, 410
[9] Wagner, *Zeitsch. physikal. Chem.*, 1890, 5, 31 ; Simeon, *Phil. Mag*, 1914, [6] 95 ; Walker, *ibid.*, 288 ; Linde, *Zeitsch. Elektrochem.*, 1923, 29, 163.
[10] Timberg, *Wied. Annalen*, 1887, 30, 545.
[11] Kohlrausch and Grüneisen, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1 MacGregory, *Wied. Annalen*, 1894, 51, 126 ; Jones and Chambers, *loc. cit.* ; Jones Getman, *Zeitsch. physikal. Chem.*, 1903, 46, 265 ; 1904, 49, 400.
[12] Schumann, *Wied. Annalen*, 1887, 31, 32.
[13] Gladstone, *Trans. Chem. Soc.*, 1891, 59, 589 ; Jones and Getman, *Zeitsch. phys Chem.*, 1904, 49, 400.
[14] Marignac, *Ann. Mines*, 1856, [5], 9, 3.
[15] van 't Hoff, Kenrick, and Dawson, *Zeitsch. physikal. Chem.*, 1902, 39, 27.
[16] Thomsen, *J. prakt. Chem.*, 1877, 16, 97, 323.
[17] Pickering, *Ber.*, 1894, 27, 67.
[18] van 't Hoff, Kenrick, and Dawson, *loc. cit.* ; Thomsen found −4 310 *Thermochemistry*, English translation by Burke (Longmans, Green & Co.), 1908, p. 50
[19] Pickering, *loc. cit.* ; Person (*Ann. Chim. Phys.*, 1849, [3], 27, 251) found 40·7 cal. per gram-equivalent to 8·913 Cal. per gram-molecule.
[20] Tammann, *Ann. Phys.*, 1899, [3], 68, 553.
[21] Lefèbvre, *Compt rend.*, 1860, 70, 684.
[22] Hammerl, *Sitzungsber. K. Akad. Wiss. Wien*, 1875, 72, 667.

which belongs to the rhombic system. It can be obtained by repeated fusion of the hexahydrate. The unstable β-form separates in large transparent plates on cooling a solution containing more than one molecule of calcium chloride to six molecules of water.

Pressure in kgm	Melting-point, ° C.	Pressure in kgm.	Melting-point, ° C.
1	29·70	2000	50·56
500	35·76	2500	55·41
1000	40·08	3000	59·96
1500	45·40		

Calcium Chloride Dihydrate, $CaCl_2.2H_2O$, may be obtained by the addition of hydrochloric acid to an aqueous solution of calcium chloride.[1]

Calcium Chloride Monohydrate, $CaCl_2.H_2O$, was first described by Roozeboom. As the vapour pressure of saturated calcium chloride solution, and, therefore, of the solid phase, is greater than one atmosphere at 175·5° C., the transition-point of the di- into the mono-hydrate, it is evident that, to obtain the latter, a higher hydrate must be heated under pressure, otherwise the anhydrous salt will be obtained.

Calcium chloride is obtained in large quantities as a waste product from certain industrial processes, notably the ammonia-soda process, the Weldon recovery process, and the manufacture of potassium chlorate. Many proposals have been made for its utilisation—for example, in the manufacture of pearl-hardening, as a metallurgical flux, or as a source of chlorine. For the latter purpose it may be heated with sand or clay under various conditions. So far, however, not much practical success has been attained.[2] It may also be used for the production of chlorate electrolytically.[3]

A few minor uses have been found for calcium chloride, for instance ⸴ a refrigerating agent, and, owing to its hygroscopic nature, for the ⸴ying of dust.

Addition Compounds.—Calcium chloride forms, with ammonia, four fferent compounds in which 1 molecule of the salt is combined with 4, 2, and 1 molecules of ammonia respectively.[4] Hüttig has studied ⸴ dissociation pressure of ammonia at different temperatures and the ⸴at of formation for all these compounds.[4] Similar compounds, some- ⸴es hydrated, are formed with a number of amino-compounds:—for ample, with phenylhydrazine[5] and aniline,[6] with acetamide,[7] with ⸴iocarbamide,[8] with carbamide and asparagine,[9] and with α-amino-acids

[1] Ditte, *Compt. rend.*, 1881, **92**, 242; *Ann. Chim. Phys.*, 1881, [5], **22**, 558.
[2] Lunge, *Sulphuric Acid and Alkali* (Gurney and Jackson), 1895, vol. ii., p. 430; ⸴6, vol. iii., pp. 124, 350, 369, 584.
[3] See Calcium Chlorate, p. 47
[4] Hüttig, *Zeitsch. anorg. Chem.*, 1922, **123**, 31. See also Isambert, *Compt. rend.*, 78, 86, 968; Rose, *Ann. Chim. Phys.*, 1836, [2], **62**, 315.
[5] Moitessier, *Compt. rend.*, 1898, **127**, 722.
[6] Tombeck, *Ann. Chim. Phys.*, 1900, [7], **21**, 383.
[7] Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1415; Kusnetzoff, *ibid.*, 1909, ⸴ 379.
[8] Rosenheim and Meyer, *Zeitsch. anorg. Chem.*, 1906, **49**, 13.
[9] Okuda and Fujiwaka, *J. Tokyo Chem. Soc.*, 1919, **40**, 404, see *J. Chem. Soc.*, 1920, 3, Abs. i, 150.

and polypeptides.[1]   It has been suggested that the compound with carbamide, $CaCl_2.4CO(NH_2)_2$, which is stable in air and soluble in water, and has a melting-point of 158°–160° C., might be of value in subcutaneous injections for hay fever and asthma.[2]

Calcium chloride forms addition compounds with the alcohols. On evaporating a solution in ethyl alcohol at a low temperature rectangular plates of $2CaCl_2.7C_2H_5OH$ are deposited.   The compounds $CaCl_2.3C_2H_5OH$ [3] and $CaCl_2.CH_3OH$ [4] have also been separated, as well as a mono- and a di-acetone compound,[5] and compounds with isobutyl and amyl alcohols.[3]

Antonow obtained a number of addition compounds with hydroxylamine,[6] $2CaCl_2.3NH_2OH.6H_2O$, $2CaCl_2.5NH_2OH.4H_2O$, $CaCl_2.2NH_2OH.$ $2H_2O$, $CaCl_2.2NH_2OH.H_2O$, $CaCl_2.2NH_2OH$, $4CaCl_2.NH_2OH.20H_2O$, and $CaCl_2.3NH_2OH.HCl$.

Double Salts.—Calcium chloride forms a number of double salts with other chlorides.   A list is given below :—

Salt	Remarks.	Authority.
$4NaCl.CaCl_2$ . .	Not separated. Existence supposed from heat of solution of mixed salts.	Berthelot and Ilosvay, *Ann. Chim. Phys.*, 1883, [5], **29**, 295.
$KCl.CaCl_2$ . .	Melting-point, 754° C.	Menge, *Zeitsch. anorg. Chem.*, 1911, **72**, 162.
,, . .	Melting-point, 740° C.	Moldenhauer and Andersen, *Zeitsch Elektrochem.*, 1913, **19**, 444.
$2KCl.CaCl_2$ . .	. .	Berthelot and Ilosvay, *loc. cit.*
$2KCl.3CaCl_2$ . .	Melting-point, 725° C.	Lantsberry and Page, *J. Soc. Chem. Ind.*, 1920, **39**, 37T.
$2CsCl.CaCl_2$. .	Slender colourless prisms.	Jamieson, *Amer. J. Sci.*, 1917, [4], **43**, 67.
$CaCl_2.BaCl_2$ . .	Melting-point, 631° C.	Schaefer, *Jahrb. Miner.*, 1914, **1**, 15.
$CaCl_2.BaCl_2.SrCl_2$. .	Melting-point, 500° C.	Schaefer, *ibid.*, 1919, Beil. Bd., **43**, 132.
$CaCl_2.ZnCl_2.5.5H_2O$ $2CaCl_2.ZnCl_2.6H_2O$ }	Hygroscopic crystals.	Ephraim and Model, *Zeitsch anorg. Chem.*, 1910, **67**, 379.
$2TlCl_3.CaCl_2.6H_2O$.	Large colourless crystals.	Gewecke, *Annalen*, 1909, **366** 217.
$PbCl_4.16CaCl_2$ . .	Decomposed in dilute solution, forming PbO_2.	Nicklès, *Ann. Chim. Phys.* 1867, [4], **10**, 323.
$5HgCl_2.CaCl_2.8H_2O$.	Decomposed by water.	{ Bonsdorff, *Pogg. Annalen*, 182, **17**, 122.
$2HgCl_2.CaCl_2.6H_2O$.	Deliquescent.	Varet, *Compt. rend.*, 1896, **12:** 421.
$2CdCl_2.CaCl_2$. $2CuCl_2.CaCl_2$. }	. .	Varet, *loc. cit.*
$CaCl_2.SnCl_4.6H_2O$.	Colourless deliquescent rhombohedra.	Topsöe, *Jahresber.*, 1874, 180.
$CaCl_2.3SeOCl_2$ . .	. .	Wise, *J. Amer. Chem. Soc.*, 1923, **45**, 1233.

[1] Pfeiffer and von Modelski, *Zeitsch. physiol. Chem.*, 1912, **81**, 329 ; 1913, **85**, 1.
[2] Knoll & Co., German Patent, 306809 (1918) ; from *Chem. Zentr.*, 1918, ii., 420.
[3] Heindl, *Monatsh.*, 1881, **2**, 200.
[4] Menschutkin, *loc. cit.*
[5] Bagster, *Trans. Chem. Soc.*, 1917, **111**, 494.
[6] Antonow, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 476.

The systems $CaCl_2 : KCl : H_2O$ and $CaCl_2 : MgCl_2 : H_2O$ have been studied at 25° C.[1]

A double compound of mercuric cyanide and calcium chloride, $2Hg(CN)_2.CaCl_2.6H_2O$, is known.[2] The appearance and gradual increase in quantity of the cyanide ion in the solution on warming leads to the conclusion that transformation to the compound $Hg(CN)_2.Ca(CN)_2.HgCl_2$, takes place.

Calcium Perchloride.—At low temperatures chlorine is more soluble in calcium chloride solution than in pure water, which may indicate the formation of a perchloride.[3] Determinations of the freezing-point lowering produced by chlorine in alkaline earth chloride solutions lead to the same conclusions.[4] No solid perchlorides of the alkaline earths have been obtained.

CALCIUM AND BROMINE.

Calcium Bromide, CaBr₂.—Calcium will combine directly with bromine vapour at red heat to produce calcium bromide.[5] The heat of formation is 169·2 Cal.[6] The salt may also be obtained by the action of bromine and a reducing agent, for example iron filings or phosphorus,[7] on calcium carbonate or hydroxide in the presence of water, or by the action of bromine on lime at red heat.[8]

It is most conveniently prepared, however, by the neutralisation of hydrobromic acid by calcium carbonate. In order to obtain the anhydrous salt in a state of purity, it must be fused in an atmosphere of hydrogen and hydrobromic acid to prevent the partial decomposition of the salt by water, and then, after removal of these gases by nitrogen at 400° C., it must be cooled in an atmosphere of nitrogen.[9] The resulting product is a white solid of density 3·353 at 25° C.[10]

Calcium bromide melts at 760° C.,[11] and sublimes at 720° C.[12]

Like the chloride the bromide is hygroscopic, and may be used as a drying agent. It may even be a little more efficient for this purpose than the former.[13]

Calcium bromide is very soluble in water, the heat of solution being 1151 Cal.[14] The following values have been found for the solubility different temperatures[15] :—

perature, ° C.	−22	−14	−7	−6	+8	+9	+11	+20	+50
ns $CaBr_2$ in 100 grams solution	50·3	52·5	52·6	52·6	53·1	55·1	55·7	57·1	62·6

Lee and Egerton, *Trans. Chem. Soc.*, 1923, **123**, 706.
Varet, *Compt. rend.*, 1895, **121**, 348.
Goodwin, *Ber.*, 1882, **15**, 3039.
Meyer, *Zeitsch. anorg. Chem.*, 1902, **30**, 115
Moissan, *Ann. Chim. Phys.*, 1899, [7], **18**, 289.
de Forcrand, *ibid.*, 1911, [8], **24**, 256.
Klein, *Annalen*, 1863, **128**, 237
Balard, *Ann. Chim. Phys.*, 1826, [2]. **32**, 337.
Richards and Hönigschmid, *J. Amer. Chem. Soc.*, 1910, **32**, 1577.
Ruff and Plato found a density of 3·4 at 20° C., *Ber.*, 1902, **35**, 3612.
Ruff and Plato, *Ber.*, 1902, **35**, 3616 ; 1903, **36**, 2357. Kellner finds 730° C., *Zeitsch. g. Chem.*, 1917, **99**, 137.
Stock and Heynemann, *Ber.*, 1909, **42**, 4088.
Baxter and Warren, *J. Amer. Chem. Soc.*, 1911, **33**, 340.
Thomsen, *J. prakt. Chem.*, 1877, [2], **16**, 323 ; de Forcrand, *loc. cit.*
Etard, *Ann. Chim. Phys.*, 1894, [7], **2**, 503.

The Hydrates of Calcium Bromide have been studied by no means so carefully as those of the chloride. A hexahydrate, $CaBr_2.6H_2O$, crystallises at the ordinary temperature and melts at 38° C.[1] Its boiling-point is 149°–150° C.[2] The heat of formation of the hexahydrate from the anhydrous salt is 25·60 Cal., and the heat of solution is −1·090 Cal.[3]

According to Curtmann,[4] the trihydrate, $CaBr_2.3H_2O$, is the salt most frequently met. It crystallises in bright colourless needles, is very hygroscopic, melts at 80° C., and dissolves in water and alcohol. Its behaviour also points to the possible existence of a compound, $2CaBr_2.5H_2O$, at 180°–181° C.

The existence of other hydrates has been reported. Kusnetzoff[5] prepared the tetrahydrate, $CaBr_2.4H_2O$, transition temperature from the hexahydrate 55° C., and, later, by hot centrifuging, he obtained a dihydrate, $CaBr_2.2H_2O$.[6]

Guareschi[7] stated that hydrates, containing 6, 5, 4, 3, 1½, 1, and ½ molecules of water respectively, can be obtained by keeping the bromide under varying conditions of temperature and pressure of water vapour until constant weight is attained.

Addition Compounds.—Calcium bromide unites directly with ammonia. Four compounds are known, $CaBr_2.8NH_3$, $CaBr_2.6NH_3$, $CaBr_2.2NH_3$, and $CaBr_2.NH_3$. The heats of formation and the dissociation pressures have been studied.[8] Like calcium chloride it also combines with aniline,[9] with carbamide and asparagine,[10] and with phenylhydrazine.[11]

Calcium bromide dissolves readily in absolute alcohol, and from the solution tabular rhombic crystals may be obtained having the composition $CaBr_2.3C_2H_5OH$.[12] The compound is hygroscopic and is decomposed by heat with the formation of lime, hydrobromic acid, and ethyl bromide.

Double Salts.—A double bromide of calcium and manganese, forming pink crystals of composition $CaBr_2.MnBr_2.4H_2O$, has been described.[13] Calcium bromide also combines with mercuric cyanide to give the compound $2Hg(CN)_2.CaBr_2.7H_2O$. The heat of formation from the two solid salts and liquid water is 40·47 Cal.[14] A double bromide of mercury and calcium, $HgBr_2.CaBr_2$, apparently existing in two forms, has been described.[15]

Freezing-point curves of mixtures of calcium bromide with sodium bromide and with potassium bromide indicate the existence of compounds $2CaBr_2.NaBr$, and $CaBr_2.KBr$.[16]

[1] Richards and Hönigschmid, *Zeitsch. anorg. Chem.*, 1898, 18, 386.
[2] Lubarski, *J. Russ. Phys. Chem. Soc.*, 1896, 28, 460.
[3] Thomsen, *J. prakt. Chem.*, 1877, 16, 97, 323.
[4] Curtmann, *J. Amer. Chem. Soc.*, 1894, 16, 621.
[5] Kusnetzoff, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 367.
[6] Kusnetzoff, *Chem. Zentr.*, 1913, i., 765.
[7] Guareschi, *Atti R. Accad. Sci. Torinò*, 1913, 48, 929.
[8] Hüttig, *Zeitsch. anorg. Chem.*, 1922, 123, 31. See also Rammelsberg, *Pogg. Ann*, 1842, 55, 239.
[9] Tombeck, *Ann. Chim. Phys.*, 1900, [7], 21, 383.
[10] Okuda and Fujiwaka, *J. Tokyo Chem. Soc.*, 1919, 40, 404; see *J. Chem. Soc.*, 1 118, Abs. i., 150.
[11] Moitessier, *Compt. rend.*, 1898, 127, 722.
[12] Roques, *J. Pharm. Chim.*, 1895, [6], 1, 301.
[13] Ephraim and Model, *Zeitsch. anorg. Chem.*, 1910, 67, 376.
[14] Varet, *Compt. rend.*, 1895, 121, 398.
[15] Bonsdorff, *Pogg. Annalen*, 1830, 19, 342.
[16] Kellner, *Zeitsch. anorg. Chem.*, 1917, 99, 137.

Calcium Perbromide.—According to Herz and Bulla,[1] variations with concentration, of the distribution coefficient of bromine between calcium bromide solution and carbon tetrachloride, indicate the existence of addition compounds of bromine and calcium bromide. Assuming that only the tetrabromide, $CaBr_4$, is formed, the dissociation constant at

25° C. $\dfrac{[CaBr_2] \times [Br_2]}{[CaBr_4]} = 0.04$ approx.[2] for a $\frac{1}{10}$ molar solution of calcium

bromide when the concentrations are measured in gram-molecules per litre.

It has also been stated that, by warming calcium bromide with one molecular-equivalent of bromine, a reddish-brown liquid, which deposits deep red crystals, is obtained. These crystals lose bromine vapour very rapidly and give white calcium bromide.[3]

CALCIUM AND IODINE.

Calcium Subiodide, CaI or Ca_2I_2.[4]—Wohler and Rodewald,[5] applying to the production of the subiodide the method already described under the subfluoride and the subchloride, heated together atomic proportions of calcium and iodine in a steel tube at 800° C. When the product was rapidly cooled in solid carbon dioxide and washed with carbon disulphide, brown hygroscopic crystals were obtained. Slow cooling resulted in the formation of a mixture of calcium iodide and metallic calcium.

Calcium Iodide, CaI_2.—Molten calcium will combine directly with iodine vapour to form the iodide.[6] The heat of formation is 141.0 Cal.[7] The salt may be prepared by the action of hydriodic acid on lime or pure marble, or, instead of the acid, iodine and a reducing agent may be used —for example, iron filings or phosphorus.[8] It can also be obtained by reduction of calcium sulphate to sulphide with carbon and addition of iodine to the aqueous extract until the colour persists.[9] To obtain the salt in the anhydrous state it must be dried in a current of dry nitrogen.[10] When heated in air it gives up all its iodine and the oxide is left.[11]

The density of the fused salt is 3.956 at 25° C.[12] The melting-point is 740° C.[13]

Calcium iodide is very hygroscopic and dissolves in water and alcohol. The heat of solution in water is 28.12 Cal.[14]

[1] Herz and Bulla, *Zeitsch. anorg. Chem.*, 1911, **71**, 254.
[2] Recalculated from Herz and Bulla's data.
[3] Meyer, *Zeitsch. anorg. Chem.*, 1902, **30**, 113.
[4] See Calcium Subfluoride, p. 24.
[5] Wohler and Rodewald, *Zeitsch. anorg. Chem.*, 1909, **61**, 54.
[6] Moissan, *Ann. Chim. Phys.*, 1899, [7], **18**, 289.
[7] de Forcrand, *ibid.*, 1911, [8], **24**, 256 ; 141.3 Cal. according to Guntz and Bassett, *Compt. rend.*, 1905, **140**, 863.
[8] Liebig, *Annalen*, 1862, **121**, 222.
[9] Liès-Bodart and Jobin, *Ann. Chim Phys.*, 1858, [3], **54**, 363.
[10] Moissan, *loc. cit.* (footnote).
[11] Schultze, *J. prakt. Chem.*, 1880, [2], **21**, 419.
[12] Baxter and Brink, *J. Amer. Chem. Soc.*, 1908, **30**, 46 ; Ruff and Plato found 4.9 at 0° C., *Ber.*, 1902, **35**, 3612.
[13] Ruff and Plato, *Ber.*, 1903, **36**, 2357.
[14] de Forcrand, *Compt. rend.*, 1911, **152**, 27 ; Thomsen found 27.7 Cal., *J. prakt. Chem.*, 1877, [2], **16**, 323.

Etard found the following values for the solubility at different temperatures [1] :—

Temperature, ° C.	−22	+7	+10	+19	+51	+64	+130	+248
Grams CaI_2 in 100 grams solution	61·6	65·0	65·1	66·3	69·4	75·9	81·3	87·1

The Hydrates of Calcium Iodide.—The deliquescent nature of the hydrated salt has led to some doubt as to the exact composition of the hydrate stable at the ordinary temperature. Tassilly gave the formula $CaI_2.8H_2O$,[2] but it is generally considered to be a hexahydrate. It crystallises in long deliquescent needles which melt at 42° C., forming a lower hydrate.[3] In this connection it might be noted that Kremers observed a break in the solubility curve between 40° and 43° C., indicating a transition-point.[4] The boiling-point of the hexahydrate is about 160° C.[5] It dissolves in water with the evolution of 1·730 Cal.[6]

Kusnetzoff mentions a tetrahydrate, $CaI_2.4H_2O$, transition temperature 65° C., and also a heptahydrate, $CaI_2.7H_2O$, which passes into the hexahydrate between −1° and +2° C.[7]

A trihydrate, $CaI_2.3H_2O$, melting below 100° C., has also been described.[8]

Addition Compounds.—Addition compounds, containing 1, 2, 4, and 6 molecules of ammonia respectively, are known. The hexammonia compound exerts a dissociation pressure of 50 mm. at 96° C., and the heat of formation from ammonia and calcium iodide is 13·63 Cal.[9] According to Huttig, however, the ammonia compounds contain 1, 2, 6, and 8 molecules of ammonia per molecule of calcium iodide.[10]

Like the chloride and bromide, calcium iodide also forms addition compounds with various organic derivatives of ammonia. Tombeck combined it with aniline, and Okuda and Fujiwaka with carbamide and asparagine.[11] Spitz [12] also obtained a compound with carbamide as well as compounds with glycine, glycyl glycine, and alanine.

Double Salts.—Several double iodides of calcium and mercury have been described; for example, $CaI_2.HgI_2.8H_2O$, $CaI_2.5HgI_2.8H_2O$, $3CaI_2.4HgI_2.24H_2O$.[13] The first dissolves in water and many solvents without decomposition, but the others are readily d by many solvents with the separation of mercuric iodide.

With zinc iodide the compound $CaI_2.ZnI_2.8H_2O$ has been and with lead the salt $CaI_2.2PbI_2.7H_2O$.[15]

Periodides of Calcium.—By the spontaneous decomposition of double iodide of lead and calcium when left in contact with its satura

[1] Etard, *Ann. Chim Phys*, 1894, [7], **2**, 503.
[2] Tassilly, *Compt. rend.*, 1896, **122**, 82.
[3] Lubarski, *J. Russ. Phys. Chem. Soc.*, 1896, **28**, 460.
[4] Kremers, *Pogg. Annalen*, 1858, **103**, 65.
[5] Lubarski, *loc. cit.*
[6] Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 38.
[7] Kusnetzoff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 367.
[8] Curtmann, *J. Amer. Chem. Soc.*, 1894, **16**, 621.
[9] Biltz, *Zeitsch. Elektrochem.*, 1920, **26**, 374.
[10] Hüttig, *Zeitsch. anorg. Chem.*, 1922, **123**, 31.
[11] See Addition Compounds of Calcium Chloride, p. 33.
[12] Spitz, *Chem. Zentr.*, 1920, ii, 601.
[13] Duboin, *Compt. rend.*, 1906, **142**, 395, 573.
[14] Ephraim and Model, *Zeitsch. anorg. Chem.*, 1910, **67**, 379.
[15] Mosnier, *Ann. Chim. Phys*, 1897, [7], **12**, 374; *Compt. rend.*, 1895, **120**, 444

aqueous solution, red crystals are obtained, corresponding in composition to a tri-iodide, $CaI_3.15H_2O$.[1]

By fusing together at 70°–80° C. an equimolecular mixture of calcium iodide and iodine, a black melt is obtained which gives crystals with a greenish lustre when cooled.[2] Even at 100° C. there is practically no pressure of iodine vapour, which seems to justify the assumption that a compound, calcium tetraiodide, CaI_4, has been formed. By fusing with 2, 3, and 4 molecules of iodine, crystalline masses are obtained of composition CaI_6, CaI_8, and CaI_{10} respectively, and similar in appearance to the tetraiodide. These also have a very small iodine vapour pressure.

The existence of a tetraiodide in aqueous solution is confirmed by freezing-point determinations.[2] The lowering is, in fact, somewhat less than for an equivalent quantity of iodide, which would indicate either that the degree of dissociation or the degree of hydration of the tetraiodide is less than that of the iodide. 8·062 grams of iodine dissolve in 100 c.c. of a 10 per cent. solution of calcium iodide at 13·5° C. Carbon bisulphide or chloroform will remove iodine from either the solid or the solution. The dissociation constant of the poly-iodides of calcium has been determined by finding the distribution of iodine between carbon tetrachloride and aqueous solutions of calcium iodide.[3] The dissociation constant is much less than in the case of the bromide and tends to diminish with increasing quantities of iodine. For an approximately $\frac{1}{10}$ molar solution of calcium iodide, the value of "k," the dissociation constant of the tetraiodide, is in the neighbourhood of 0·0008 at 25° C., when all the concentrations are expressed in gram-molecules per litre.[4]

Mixed Halides of Calcium.—Defacqz[5] obtained several mixed halide compounds of the alkaline earths. Among them were calcium fluorochloride, $CaF_2.CaCl_2$, density 3·07; calcium fluorobromide, $CaF_2.CaBr_2$, density 3·15; and calcium fluoro-iodide, $CaF_2.CaI_2$. The latter is a deliquescent substance which was not obtained in a pure state. The fluorochloride is not stable at its melting-point.[6]

Mixed Perhalides of Calcium.—Iodine dissolves more readily in ~~ons of calcium chloride, bromide, and iodide than in pure water, ~~bly due to the formation of perhalogen compounds in solution.[7]

Solvent.	Water.	10 per cent. solution of		
		$CaCl_2$.	$CaBr_2$.	CaI_2.
~~emperature, ° C. .	Ordinary temp.	18·5	13·5	13·5
~~rams iodine per 100 c.c. of solution. .	0·0142	0·078	0·274	8·062

~~snier, *loc. cit.*
[2] Meyer, *Zeitsch. anorg. Chem.*, 1902, **30**, 113.
[3] Herz and Bulla, *ibid.*, 1911, **71**, 254.
[4] Recalculated from Herz and Bulla's data. See Calcium Perbromide.
[5] Defacqz, *Ann. Chim. Phys.*, 1904, [8], **1**, 337; see also Poulenc, *ibid.*, 1894, [7], **2**, 24.
[6] Plato, *Zeitsch. anorg Chem.*, 1907, **58**, 363.
[7] Meyer, *Zeitsch. physikal. Chem.*, 1902, **30**, 113.

It will be noticed that the tendency to polyhalide formation is by far the greatest in the case of the iodide. Bromine is also taken up in considerable quantity.

Determinations of the freezing-point lowering in aqueous solutions seem to indicate the possibility of the formation of the compound $CaBr_4I_2$.

OXYHALOGEN DERIVATIVES OF CALCIUM.

Calcium Oxychloride.—On fusing calcium chloride in moist air it becomes basic, due to the formation of an oxysalt, $CaCl_2.CaO$.[1] On prolonged heating it forms calcium oxide. When calcium chloride solution is boiled with slaked lime and the liquid filtered, white needle-shaped crystals of calcium oxychloride separate out. These are stable out of contact with air, lose part of their water of crystallisation over sulphuric acid, absorb carbon dioxide from the air, and are decomposed by water and alcohol. Various formulæ have been given to the compound, for example: $3CaO.CaCl_2.15H_2O$,[2]　$2CaO.CaCl_2.15H_2O$,[3]　$3CaO.CaCl_2.14H_2O$,[4]　and $3CaO.CaCl_2.16H_2O$.[5] The formula of the partially dehydrated salt has been given as $CaCl_2.3CaO.3H_2O$,[5] and also as $CaCl_2.2CaO.H_2O$.[6] Schreinemakers and his colleagues,[7] however, have carefully studied the system, CaO : $CaCl_2$: H_2O, under varying conditions of temperature and concentration, and their results indicate the existence of the following compounds: at 10° and 25° C., $CaCl_2.3CaO.16H_2O$ and $CaCl_2.CaO.2H_2O$; at 50° C., $CaCl_2.CaO.2H_2O$ and $CaCl_2.CaO.3H_2O$; and also $CaCl_2.4CaO.14H_2O$.

An oxychloride of lead and calcium, $2PbO.CaCl_2.CaO$, is obtained by dissolving lead oxide in boiling calcium chloride solution.[8] By the action of a solution of calcium chloride on mercuric oxide a compound $CaCl_2.2HgO.4H_2O$ is formed.[9]

Calcium Hypochlorite, $Ca(OCl)_2.4H_2O$, may be obtained in feather-like crystals by freezing a solution of bleaching powder and carefully thawing the cryohydrate on a filter,[10] or by evaporating solution of bleaching powder over sulphuric acid *in vacuo*. Tiesenholt[11] tried to obtain it by the action of chlorine monoxide dry calcium hydroxide, but the product was not pure because the did not take up its equivalent of acid anhydride.

In 1906 the Griesheim Elektron Company took out a patent[1] the manufacture of calcium hypochlorite by treating cold milk

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[1] Gorgeu, *Compt. rend.*, 1884, **99**, 256.

[2] Grimshaw, *Chem. News*, 1874, **30**, 280 ; Zahorsky, *Zeitsch. anorg. Chem.*, 1893, **3,**

[3] Rose, *Dingl. poly. J*, 1873, **209**, 204 ; *Pogg. Annalen*, 1854, **93**, 612 ; Göp *Schweigger's J.*, **29**, 155.

[4] Beesley, *Jahresber.*, 1850, 299.

[5] André, *Compt. rend.*, 1881, **92**, 1452 ; *Ann. Chim. Phys.*, 1884, [6], **3**, 66.

[6] Ditte, *Compt. rend.*, 1880, **91**, 576

[7] Schreinemakers and Milikan, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15,** from *J. Chem. Soc.*, 1912, **102**, Abs. ii., 760; Schreinemakers and Figee, *Chem. Week'* 1911, **8**, 683 ; see also Milikan, *Zeitsch. physikal. Chem.*, 1916, **92**, 59 ; 1917, **92**, 496.

[8] André, *Compt. rend.*, 1887, **104**, 359.

[9] Klinger, *Ber.*, 1883, **16**, 997 ; André, *Compt. rend.*, 1887, **104**, 431.

[10] Kingzett, *Chem. News*, 1875, **31**, 113 ; **32**, 22 ; 1882, **46**, 120 ; *J. Chem. Soc.*, 1 **28**, 404.

[11] von Tiesenholt, *J. prakt. Chem.*, 1902, [2], **65**, 512.

[12] Griesheim Elektron Company, German Patent. 188524. April 27. 1906.

lime with chlorine. By evaporation *in vacuo* a crystalline hypochlorite is first formed. This is washed and dried *in vacuo* to remove the water of crystallisation, as the salt is more stable in the anhydrous state. Under certain conditions basic hypochlorites may be formed. Two have been isolated of composition $Ca(OCl)_2.2Ca(OH)_2$, and $Ca(OCl)_2.4Ca(OH)_2$. The commercial anhydrous hypochlorite, known by the trade name of " Hyporit," is more stable than ordinary bleaching powder. It gives a clear solution in water and contains 80 to 90 per cent. of bleaching chlorine. The solution smells strongly of chlorine monoxide. It can be stabilised by introducing lime to the extent of 25 to 30 per cent. This settles to the bottom as " lime sludge," and, mixed with a certain amount of fresh lime, can be used for increasing the stability of a further quantity of solution. Magnesium hydroxide cannot replace the lime for this purpose.[1] The stability is not much influenced by concentration and temperature.

Vincent and Gaillard [2] pointed out that, as a purifying agent for drinking-water, calcium hypochlorite had certain practical advantages over alkali hypochlorites, because it could be conveniently used in compressed tablets. A litre of water, treated with a tablet containing 3·5 mgm. of available chlorine, should be ready for drinking twenty minutes after the addition.

Bleaching Powder, CaCl(OCl).—By the action of chlorine on slaked lime, a product is obtained which is of considerable commercial importance on account of its bleaching and oxidising power in the presence of a weak acid such as carbonic acid. This is the substance known as bleaching powder.

In 1798, Charles Tennant, with a view to obtaining some cheaper bleaching agent than the expensive *Eau de Javelle*—made by the action of chlorine on caustic potash—passed chlorine into milk of lime. In the next year, however, he experimented successfully with dry slaked lime, patented the process, and began the manufacture immediately.

The method now employed for chlorinating the lime depends on the concentration of the chlorine gas available. Where the concentration of gas is high, as in the case of the chlorine obtained by the Weldon
The considerable heat is generated by the reaction, and large leaden
40° C.[13] ft. high, 10 to 20 ft. wide, and about 100 ft. long, are
Calcium loss of heat by radiation. The best temperature for the
is 30° to 40° C. The slaked lime should be of good quality
best lime for the purpose is obtained from Buxton limestone) and,
according to Lunge and Schäppi,[3] should contain 3·5 per cent. of water
above that required for the formation of hydroxide. It is spread on the
halt or flagstone floor of the chamber to a thickness of 3 to 4 inches
raked into furrows by wooden rakes. Chlorine is introduced and
for some time. The progress of absorption can be followed by
observing the diminution in colour by means of two glass windows
placed opposite to one another. The gas is also tested from time to
and the doors of the chamber must not be opened until the test
shows less than $2\frac{1}{2}$ grains of chlorine per cubic foot. The last of the
chlorine may be removed by blowing in fine lime dust. Twelve to

Griffin and Hedallen, *J. Soc. Chem. Ind.*, 1915, **34**, 530.
Vincent and Gaillard, *Compt. rend.*, 1915, **160**, 483; see also Michaelis, *Münch. med. Woch.*, 1919, **66**, 45; from *J Chem. Soc.*, 1919, **116**, Abs. ii., 155.
Lunge and Schäppi, *Dingl. poly. J.*, 1880, **237**, 63.

twenty-four hours are required for absorption. With a thick layer of lime it may be necessary to rake it over and re-chlorinate. The chambers may be arranged in series, so that the fresh gas comes into contact with nearly chlorinated lime, and fresh lime with nearly spent gas.

For dilute chlorine, such as that from the Deacon process containing as much as 90 per cent. of inert gases, the same precautions for keeping down the temperature are not necessary. The lime is therefore laid in layers, a little more than half an inch thick, on shelves of slate or sandstone 6 inches apart, set into the walls of the chambers in such a way that they are 6 inches short at alternate ends. The gas thus zig-zags through the chamber, passing over each shelf in succession. The chlorine is circulated through a battery of chambers.

In 1888 Hasenclever patented a process by which the lime is driven, by means of a worm screw, through a cylindrical leaden chamber, meeting on its way a counter-current of chlorine. After passing through a succession of these cylinders, the finished lime drops directly into the packing cask, thus greatly reducing the risk to workmen through coming into contact with chlorine and bleaching-powder dust.

Improvements in bleaching-powder manufacture lie mainly in the direction of the use of mechanical appliances in place of hand-work.[1]

The final product, which should be a heavy powder, nearly white, and capable of being kneaded by the fingers into a sort of dough, must be carefully packed in hard-wood casks or mild steel drums in such a way as to prevent access of light, heat, moisture, or carbon dioxide, which all, especially light, cause rapid decomposition. The presence of free lime helps to stabilise the powder, and, for use in hot countries, it is apparently advantageous to mix it with 20 per cent. of quicklime.[2]

The Properties of Bleaching Powder.—Bleaching powder is a white powder smelling of chlorine and chlorine monoxide, owing to the gradual loss of these gases. This loss results in a diminution of available chlorine, which is also brought about by transformation into chlorate. A good commercial powder contains 36-38 per cent. of available chlorine. It is only slightly hygroscopic. On treating with water chloride and hypochlorite are formed in solution and a residue is left.

By heating to 100° C. about half the water which the contains is lost, most of the remainder is removed at 150° C traces only at red heat. By heating in the pre chlorine is set free at 70° C. Above this temp with a trace of chlorine monoxide, is obtained.[3] A. ll bleaching chlorine is destroyed.[4] Dilute acids liberate chlorine from If the liquid is very dilute, hypochlorous acid is obtained. On boiling solution of bleaching powder, oxygen is given off and a small quan of chlorate formed.[5]

Ammonium salts are oxidised to nitrogen on boiling in solution bleaching powder.[6]

$$2NH_3 + 3CaOCl_2 = 3CaCl_2 + 3H_2O + N_2.$$
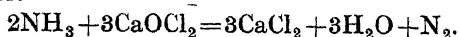
[1] Montgomery, *Chem. Met. Eng.*, 1922, **26**, 1038.
[2] Rettie, Smith, and Ritchie, *J. Soc. Chem. Ind.*, 1918, **37**, 311T ; MacCulloch, ? 1921, **40**, 240T.
[3] Lunge, *Zeitsch. anorg. Chem.*, 1892, **2**, 311 ; Lunge and Schoch, *Ber.*, 1887, **20**, 1
[4] Ditz, see references under Constitution, p. 43.
[5] Lunge, *J. Soc. Chem. Ind.*, 1885, **4**, 722.
[6] Kolb, *Ann. Chim. Phys.*, 1867, [4], **12**, 266.

Certain metallic oxides, such as those of cobalt, nickel, iron, manganese, and copper, react catalytically upon bleaching powder solution, causing a vigorous evolution of oxygen.[1]   The metals, iron, tin, copper, nickel, and cobalt, also have the same effect.[2]

Bleach Liquor.—Instead of bleaching powder, bleach liquor, as first obtained by Tennant by the action of chlorine on milk of lime, is sometimes prepared by alkali works for use in bleaching works which are not too far away.   It may also be made by extracting bleaching powder with water.

Bleaching powder solution has valuable germicidal properties, and has long been used as a disinfectant.   One part of bleaching powder in 2000 parts of sewage will free it from typhoid bacilli and cholera spores in two hours.   Anthrax spores require a 1 per cent. solution.[3]

Other Uses of Bleaching Powder.—Apart from the value of its bleaching and antiseptic properties, bleaching powder is also a useful chlorinating agent in the laboratory and in industry, for example in the production of chloroform from alcohol or acetone.[4]

It may be used in the laboratory as a source of chlorine or oxygen.[5]

The Constitution of Bleaching Powder.—The composition of bleaching powder corresponds approximately to a mixture of equivalent proportions of calcium chloride and hypochlorite with a certain amount of water and free lime ; but whether it is actually to be regarded as consisting mainly of a compound of formula $CaCl(OCl)$ or $CaCl_2.Ca(OCl)_2$, or simply as a mixture, is still a vexed question.   The literature on the subject is very extensive.

The first suggestion put forward is indicated by the popular name " chloride of lime."   Berthollet regarded bleaching powder as formed by the direct combination of chlorine with lime.[6]   Berzelius considered it to be a compound of an oxygen acid of chlorine.   This view was soon abandoned for that adopted by Balard[7] and Gay-Lussac,[8] namely, that it is a mixture of chloride and hypochlorite.   Fresenius modified this to account for the lime, and suggested that a basic chloride is present.[9] Other variants of the mixture formula were offered.[10]   The great drawback to these was the fact that they generally allowed less bleaching than can be obtained from a good powder.

The according to Kraut,[11] a mixture of chloride and pure hypochlorite $40°$ C.[13] the action of chlorine monoxide on calcium oxide) has Calcium ies as chloride of lime, notably carbon dioxide sets is $30°$ to

best lime for the 65, 134, 64 ; Bottger, *J. prakt. Chem.*, 1865, [1], **95**, 375 ;

mayton, *ibid.*, 1896, **15**, 320.

lin, *Industrial and Manufacturing Chemistry, Organic* (Crosby Lockwood & Son), 1920, pp. 377 and 378.

For further information on the manufacture and uses of bleaching powder see *Dictionary of Applied Chemistry* (Longmans, Green & Co.), 1921, vol. i., p. 202 ; *Industry, Inorganic* (Crosby Lockwood & Son), 1917, vol. i., p. 391 ; *Chemistry* (Monographs on Industrial Chemistry) (Baillière, Tindall &

ens, *Ann. Chim. Phys.*, 1836, [2], **61**, 293.

id., 1834, [2], **57**, 225.

sac, *ibid.*, 1842, [3], **5**, 273.

hius, *Annalen*, 1861, **118**, 317

Kolb, *Ann. Chim. Phys.*, 1867, [4], **12**, 266 ; Dreyfus, *Bull. Soc. chim.*, 1884, [2], 90 ; Stahlschmidt, *Dingl. poly. J.*, 1876, **221**, 243, 335.

Kraut, *Annalen*, 1882, **214**, 354 ; 1883, **221**, 108.

free all the chlorine, the hypochlorous acid first formed acting upon the calcium chloride. He therefore favoured the Balard and Gay-Lussac formula. Schwarz,[1] on the contrary, asserted much later that the synthetic bleaching powder only gives up, under the influence of a dilute acid, an amount of chlorine corresponding to the hypochlorite present.

Von Tiesenholt [2] supported the mixture hypothesis on the grounds of the reversibility of the equation

$$2Ca(OH)_2 + 2Cl_2 \rightleftharpoons Ca(OCl)_2 + CaCl_2 + 2H_2O.$$
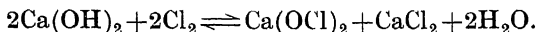
This reversibility also explained why it is impossible to prepare a bleaching powder containing the theoretical amount of available chlorine.

Winteler [3] studied the formation of bleaching powder from the point of view of the mass action law. Dry chlorine does not react with dry lime, but the process is influenced by the reversible reaction in the liquid phase between chlorine and water,

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$
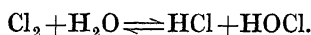
Both acids are then supposed to act upon the lime, but whether to form a compound or a mixture of basic salts the author was apparently uncertain. A large concentration of hydroxyl ions in the liquid phase favours the evolution of oxygen, which is undesirable. This explains why calcium hydroxide, the least soluble of the alkaline hydroxides, is the most suitable for the formation of bleaching powder.

The properties of bleaching powder scarcely seem to be in harmony with the view that free calcium chloride is present. Carbon dioxide will not react with calcium chloride. Bleaching powder is not very deliquescent, and can be completely dehydrated at a lower temperature than is possible in the case of the chloride.[4]

About the year 1860, Odling, in his *Manual of Chemistry*, put forward his theory of the chemical individuality of bleaching powder, and

represented its constitution by the formula $Ca{<}^{Cl}_{OCl}$. Kraut opposed

this [5] on the ground that a lithium bleaching powder could be obtained, whereas Odling's formula only permitted the existence of bleaching powders from divalent elements. The work of a number of investigators appeared to support Odling's formula.[6]

A one-compound formula was also suggested by Tarugi [7] He assumed the intermediate formation of a small quantity of peroxide, $CaO_2.H_2O_2$, by the action of oxygen liberated by chlorine from water. This, with hydrochloric acid, gives CaO_2Cl_2, chloride of peroxide. A bleaching powder containing 44·1 per cent. of active chlorine might have the formula $CaO_2Cl_2.H_2O$.

In recent times a plausible combination of the two opposing theories

[1] Schwarz, *Zeitsch. angew. Chem.*, 1907, 20, 138.

[2] von Tiesenholt, *Zeitsch. angew. Chem.*, 1901, 14, 675 ; *J. prakt. Chem.*, 1901, 63, 30 ; 1902, [2], 65, 512 ; 1906, [2], 73, 301 ; *J. Russ. Phys. Chem. Soc.*, 1905, 37, 834.

[3] Winteler, *Zeitsch. angew. Chem.*, 1902, 15, 773 ; 1903, 16, 32 ; *Zeitsch. anorg. Chem.*, 1903, 33, 161.

[4] Ditz, *Zeitsch. angew. Chem.*, 1902, 15, 749.

[5] Kraut, *loc. cit.*

[6] Lunge and Schäppi, *Dingl. poly. J.*, 1880, 237, 63 ; Lunge and Naef, *Annalen*, 1883, 219, 129 ; Lunge, *Zeitsch. anorg. Chem.*, 1892, 2, 312 ; 1893, 3, 351 ; O'Shea, *Trans. Chem. Soc.*, 1883, 43, 410.

[7] Tarugi, *Gazzetta*, 1904, 34, ii., 254.

has been made. Ditz [1] found that it is possible to obtain a bleaching powder giving 48·74 per cent. of available chlorine by repeated additions of a little water during chlorination at ordinary temperatures. At lower temperatures, however, although the reaction takes place with evolution of heat, a product is obtained containing a lower percentage of active chlorine. Between $-10°$ C. and $-20°$ C. there is not more than 31·9 per cent. even under the most favourable circumstances. Ditz accounted for these facts as follows: He supposed an intermediate compound to be first formed. This, in the presence of a sufficient excess of water, is decomposed into bleaching powder and free lime. The latter, in contact with fresh chlorine, again forms the intermediate compound, to be again decomposed, and so on theoretically to infinity, the quantity of free lime becoming less each time. The process may be expressed by the following equations :—

$$2Ca(OH)_2 + Cl_2 = CaO.CaClOCl.H_2O + H_2O$$
$$= Ca(OH)_2 + CaClOCl.H_2O$$
$$4Ca(OH)_2 + 3Cl_2 = CaO.CaClOCl.H_2O + 2CaClOCl.H_2O + H_2O$$
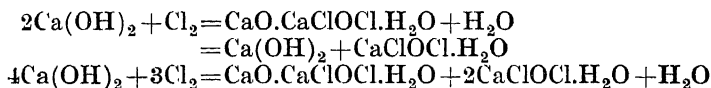
and so on, the composition of the final product being indicated by the right-hand side of the following general equation :—

$$2nCa(OH)_2 + (2n-1)Cl_2 = CaO.CaClOCl.H_2O$$
$$+ (2n-2)CaClOCl.H_2O + H_2O$$
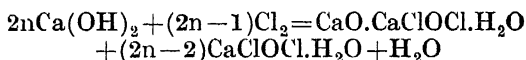
where "n" is 1, 2, 2^2, 2^3, etc. The larger the value of "n" the more complete the chlorination. At low temperatures the compound $CaO.CaClOCl.H_2O$ is stable and can indeed be isolated by chlorinating at $-15°$ C. It is also stable in dry air at $100°$ C. At a somewhat higher temperature it gives off oxygen but no chlorine. The reaction at low temperatures will tend to stop at this point, resulting in a bleaching powder of 32·4 per cent. of theoretically available chlorine. At higher temperatures hydrolysis will take place, the reaction continue with more or less readiness, and a bleaching powder containing a higher percentage of available chlorine be formed. The best theoretically possible would of course be one represented by the formula $CaClOCl.H_2O$, and contains 48·9 per cent. of available chlorine. In ordinary practice this is not obtained, so that commercial bleaching powder may be regarded obtained a mixture of this final product with a varying proportion of the intermediate basic compound.

The views of Ditz find support in the constitution of a crystalline bleaching powder obtained by Orton and Jones [2] in the form of lustrous prisms 0·5–1·2 cm. long. These, on treatment with water, formed an alkaline solution containing both chloride and hypochlorite, and left a residue consisting mainly of hydroxide. The crystals could be kept in an atmosphere free from carbon dioxide without loss of available chlorine, but the lustre gradually disappeared. They did not deliquesce in air, but after exposure calcium carbonate was present and the hypochlorite had practically disappeared, chloride and chlorate taking its place. On heating at $100°$ C., the crystals reached a constant weight at the end of an hour, but there was no diminution in the proportion of

[1] Ditz, Zeitsch. angew. Chem., 1901, 14, 3, 25, 49, 105 ; 1902, 15, 749 ; 1905, 18, 1690; 1907, 20, 754.
[2] Orton and Jones, Trans. Chem. Soc., 1909, 95, 751.

active chlorine. To conform with the results of analysis the following formulæ were suggested :—

$$2CaCl_2.2Ca(ClO)_2.9CaO(5H_2O).37H_2O,$$

or $\qquad 2(Cl.CaO.CaCl).2(OCl.Ca.OCa.OCl).5Ca(OH)_2.37H_2O.$
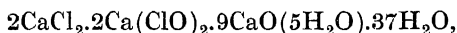
The ratio of calcium chloride to hypochlorite was constant in the crystals even when varied in the solution, but the proportion of calcium hydroxide and water was variable. The constancy of the chloride-hypochlorite ratio pointed to the existence of a compound of the two, and probably also of a basic salt. The authors supposed that the latter might be identical with the compound separated by Ditz at low temperatures. The variability of calcium hydroxide in the crystals seemed to indicate that association of the base with the compound was, partially at any rate, of the nature of an isomorphous mixture.

On the whole, the balance of evidence seems to be rather in favour of the view that bleaching powder consists essentially of the compound CaClOCl with an admixture of basic salts, but it must not be forgotten that the validity of the older chloride-hypochlorite mixture theory is still taken for granted by some authors,[1] and that certain methods by which the problem might be attacked—for example, determination of heat of formation, decomposition pressure, and so on—are practically untried.

Estimation of Available Chlorine in Bleaching Powder.—All the methods for the evaluation of bleaching powder consist essentially in the determination of the oxidising power by titration. It is most usual to titrate the bleaching-powder solution with a deci-normal arsenious oxide solution, using starch-iodide paper as an outside indicator.[2]

$$2CaClOCl + As_2O_3 = As_2O_5 + 2CaCl_2.$$
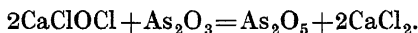
The available chlorine may also be determined by oxidising an excess of potassium iodide solution with it and estimating the liberated iodine by thiosulphate. Acetic acid is used to set free the chlorine.

$$CaClOCl + 2KI + 2CH_3COOH = Ca(CH_3COO)_2 + 2KCl + I_2 + H_2O.$$
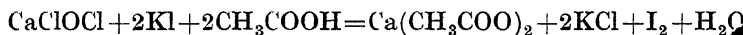
Lecomte[3] estimated the active chlorine in bleaching powder or hypochlorites by titrating the same quantity of stannous chloride with deci-normal permanganate, first in the presence of, and then in the absence of hypochlorite solution.

Calcium Chlorite, CaClO_2, is formed by the action of chlorine dioxide, ClO_2, on calcium peroxide prepared by the action of hydrogen peroxide on milk of lime. A solution is obtained from which calcium chlorite crystallises *in vacuo* over potassium hydroxide, or may be precipitated by alcohol and ether. It explodes on percussion and decomposes completely in contact with a heated wire.[4]

Calcium Chlorate, Ca(ClO_3)_2.2H_2O.—To prepare the pure salt, pure chloric acid should be neutralised with calcium carbonate or hydroxide, and the solution evaporated in the cold over sulphuric acid.[5]

[1] Higgins, *Proc. Chem. Soc.*, 1911, **27**, 67, 314 ; *Trans. Chem. Soc.*, 1911, **99**, 1912, **101**, 222 ; Taylor, *ibid.*, 1910, **97**, 2541 ; 1911, **99**, 1906 ; Taylor and Bostock, *ibid.*, 1912, **101**, 444 ; *Proc. Chem. Soc.*, 1912, **28**, 14.

[2] Carnot, *Compt. rend.*, 1896, **122**, 449.

[3] Lecomte, *Chem. Zentr.*, 1918, ii., 762 ; from *Bull. Sci. Pharmacol.*, 1918, **25**, 27.

[4] Levi, *Gazzetta*, 1922, **52**, i., 417.

[5] Wächter, *J. prakt. Chem.*, 1843, [1], **30**, 324.

The dihydrate forms rhombic crystals which are very deliquescent and melt when heated quickly to a temperature of over 100° C. On fusion, the anhydrous salt gives up oxygen with a trace of chlorine, leaving a mixture of oxide and chloride.[1] It is easily soluble in water and alcohol.

A certain amount of chlorate is formed by heating milk of lime saturated with chlorine, the quantity increasing with temperature.[2] The production of chlorate by this method was begun on the commercial scale at St. Helens in 1847. Milk of lime of specific gravity 1·08 is agitated in cylindrical cast-iron vats, 10 ft. in diameter and $5\frac{1}{2}$ ft. high, whilst chlorine is passed through. The temperature is kept at 60°–70° C. Several vats may be placed in series, and the process run on the counter-current principle. The end-point is reached when addition of a dilute acid causes no evolution of chlorine. The chlorate solution is used chiefly for the production of sodium and potassium chlorates.[3]

Calcium chlorate may also be prepared by the electrolytic oxidation of the chloride. According to Tucker and Moody,[4] the best output is obtained by the use of a 20 per cent. solution at 80° C. and an anode density of 8 amp. per sq. dcm. The platinum electrodes should be in a horizontal position and 10 cm. apart. Addition of sodium dichromate or hydroxide increases the efficiency considerably. For example, 10 per cent. of sodium hydroxide raises the efficiency from 67·4 per cent. to 83 per cent.

Calcium Perchlorate, $Ca(ClO_4)_2$.—By the neutralisation of perchloric acid by calcium carbonate or hydroxide, Sérullas[5] obtained this salt only as a syrupy mass which solidified on cooling and was soluble in water and alcohol. It can, however, be crystallised with 4 molecules of water. The crystals melt below 100° C., but the anhydrous salt is stable at 260°–270° C.[6]

Calcium Oxybromide.—When calcium bromide solution is boiled with calcium hydroxide, and the liquid is filtered and cooled, beautiful needle-like crystals separate out.[7] They are decomposed by water and alcohol, leaving lime, and their composition is represented by the formula $CaBr_2.3CaO.16H_2O$. On drying at 120° C. in an atmosphere free from carbon dioxide, a trihydrate, $CaBr_2.3CaO.3H_2O$, is formed.

Schreinemakers and Milikan,[8] investigating the system $CaBr_2 : Ca(OH)_2 : H_2O$ at 25° C., found an oxybromide $3CaBr_2.4CaO.16H_2O$ in addition to the compound $CaBr_2.3CaO.16H_2O$.

Calcium Hypobromite, $Ca(OBr)_2$, is produced in solution with the evolution of heat by the action of bromine on lime-water.[9] It has an oxidising and bleaching action, and bromine is liberated from it by

[1] Polititzin, *J. Russ. Phys. Chem. Soc.*, 1890, 22, 333.

[2] Crace-Calvert, *J. Chem. Soc.*, 1851, 3, 100; Lunge, *J. Soc. Chem. Ind.*, 1885, 4, 722.

[3] Partington, *The Alkali Industry* (Monographs on Industrial Chemistry) (Baillière, Tindall & Cox), 1918, p. 131.

[4] Tucker and Moody, *J. Soc. Chem. Ind.*, 1900, 19, 977; see also Schoop, *Zeitsch. Elektrochem.*, 1895-6, 2, 209, 227; Bischoff and Foerster, *ibid.*, 1897-8, 4, 464; Oettel, *ibid.*, 1898-9, 5, 1.

[5] Sérullas, *Ann. Chim. Phys.*, 1831, [2], 46, 304.

[6] Willard and Smith, *J. Amer. Chem. Soc.*, 1923, 45, 286.

[7] Tassilly, *Compt. rend.*, 1894, 119, 371; *Ann. Chim. Phys.*, 1899, [7], 17, 38.

[8] Schreinemakers and Milikan, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 52; see *J. Chem. Soc.*, 1912, Abs. ii, 102, 760; Milikan, *Zeitsch. physikal. Chem.*, 1916, 92, 59.

[9] Balard, *Ann. Chim. Phys.*, 1826, [2], 32, 337; Dancer, *J. Chem. Soc.*, 1862, 15, 477.

dilute acids. Although this solution is fairly stable it is decomposed by heat or sunlight.

Brome Bleaching Powder.—Berzelius first observed that bromine reacts with calcium hydroxide forming a reddish compound with bleaching properties.[1] Killby[2] has stated that brome bleaching powder contains bromine in three forms : as bromide, hypobromite, and finally, in a more loosely combined form, probably as the perbromide, thus giving the red colour. Wilks[3] regarded the reaction as an adsorption of the bromine by the lime, rather than chemical combination as between chlorine and lime.

By heating the red compound at 100° C. until no more water and bromine are driven off, there is formed a pale yellow powder containing 33 per cent. of available bromine and having substantially the composition $CaO.CaBrOBr.H_2O$, which recalls Ditz's intermediate compound (see under Bleaching Powder). This yellow product has bactericidal and bleaching properties.[4]

Calcium Bromate, $Ca(BrO_3)_2.H_2O$, is obtained by the neutralisation of bromic acid with either the hydroxide or the carbonate of calcium,[5] or by the electrolytic oxidation of calcium bromide.[6] It forms monoclinic crystals isomorphous with strontium and barium bromates.[7] It is soluble in an equal weight of cold water. At 180° C. the bromate loses its water of crystallisation, and at a still higher temperature it gives up oxygen and forms the bromide. The density of the bromate is 3·829.

Calcium Oxyiodide.—A crystalline compound, $CaI_2.3CaO.16H_2O$, has been prepared.[8] It is decomposed by water and alcohol, but is stable at 25° C. in contact with a solution containing from 28·44 per cent. to 66·68 per cent. of calcium iodide.[9] It assumes a red-violet colour under the influence of light, is less hygroscopic than the neutral iodide, and on heating it is probably dehydrated with the separation of iodine. *In vacuo*, at ordinary temperatures, water is removed and the trihydrate, $CaI_2.3CaO.3H_2O$, less unstable to light but very hygroscopic, is obtained.[8]

Calcium Hypoiodite, or Iodine Bleaching Powder.—When iodine is allowed to react with calcium hydroxide and water at the ordinary temperature, in addition to an iodide and iodate, a compound supposed to be analogous with chlorine bleaching powder is obtained in solution. It is colourless, has an odour strongly suggestive of iodoform, and, although moderately stable in the dark, is readily decomposed by heat and light. It is supposed to consist either of a mixture of hypoiodite and iodide or of the compound $CaI(OI)$.[10]

According to Wilks[11] iodine is adsorbed by slaked lime.

Calcium Iodate, $Ca(IO_3)_2$.—This salt occurs naturally in the

[1] See also Lowig, *Pogg. Annalen*, 1828, 14, 492.
[2] Killby, *Ann. Rep. Chem. Soc.*, 1910, 7, 48.
[3] Wilks, *Trans. Chem. Soc.*, 1912, 101, 366.
[4] Arthur and Killby, British Patent, 131750 (1918) ; *J. Soc. Chem. Ind.*, 1919, 8, 843A.
[5] Rammelsberg, *Pogg. Annalen*, 1841, 52, 88.
[6] Sarghel, *Zeitsch. Elektrochem.*, 1899–1900, 6, 149.
[7] Marignac, *Jahresber.*, 1857, 127.
[8] Tassilly, *Compt. rend.*, 1894, 119, 371 ; *Ann. Chim. Phys.*, 1899, [7], 17, 38.
[9] Milikan, *Zeitsch. physikal. Chem.*, 1916, 92, 59.
[10] Lunge and Schoch, *Ber.*, 1882, 15, 1883.
[11] See Brome Bleaching Powder.

nitre beds of Chili and in sea-water.[1] It can be obtained either by the action of calcium carbonate or hydroxide on iodic acid, or, since calcium iodate is not very soluble in water, by precipitating a boiling solution of calcium nitrate with an alkaline iodate. The salt crystallises with 4 or 6 molecules of water according to circumstances.[2] The hexahydrate belongs to the rhombic system. On drying at 100° C. a monohydrate is left, but it is only at a considerably higher temperature, about 200° C., that the anhydrous salt is obtained. On further heating, oxygen and iodine are given off and a mixture of iodide and oxide remains.

Calcium Periodate, $Ca(IO_4)_2$, is obtained by the action of a strong solution of periodic acid on calcium carbonate and evaporation of the still acid solution over concentrated sulphuric acid.[3]

By treating feebly acid solutions with calcium carbonate, or by allowing an alkaline periodate to react with calcium nitrate, a basic salt, $Ca(IO_4)_2.CaO.9H_2O$[4] or $3H_2O$,[5] is formed. The first method of preparation gives reddish crystals and the second white. At 170° C. the basic salt loses all its water of crystallisation, and is decomposed at a still higher temperature to form the more basic compound $Ca(IO_4)_2.4CaO$.[6]

Rammelsberg also obtained the compound $3Ca(IO_4)_2.5CaO$ as a gelatinous precipitate by the action of ammonia on a solution of the periodate.[3]

CALCIUM AND MANGANESE.

Calcium Manganites.—Crystallised manganites, of composition varying with the temperature, can be obtained by heating together calcium chloride, calcium oxide, and manganese chloride. At a bright red heat $MnO_2.2CaO$ is formed, and at lower temperatures $2MnO_2.CaO$, $3MnO_2.CaO$, and $CaO.MnO_2$.[7] Potassium permanganate with calcium chloride gives a pentamanganite, $5MnO_2.CaO$.[8]

By the action of a manganese salt on excess of calcium hypochlorite brownish precipitates of variable composition are obtained.[9] They constitute the Weldon mud produced in the regeneration of manganese dioxide in the Weldon chlorine process.[10]

Calcium Manganate is obtained by heating together lime and any manganese salt with free access of air.[11] Auger and Billy, however, assert that no true alkaline earth manganates are formed, only mangani-manganates of the general formula $R_3Mn_2O_8.H_2O$.[12]

[1] Sonstadt, *Chem. News*, 1872, **25**, 196.
[2] Ditte, *Ann. Chim. Phys.*, '90, [6], **21**, 145; see also Millon, *ibid.*, 1843, [3], **9**, 413; Marignac, *Jahresber.*, 1872, 125. See also Rammelsberg, *Pogg. Annalen*, 1838, **44**, 576.
[3] Rammelsberg, *Jahresber.*, 1868, 164.
[4] Ihre, *Ber.*, 1870, **3**, 316. Rammelsberg, *loc. cit.*
[5] Langlois, *Ann. Chim. Phys.*, 1852, [3], **34**, 257. See also Bengieser, *Annalen*, 1836, **17**, 254.
[6] See also Barium Periodate.
[7] Gorgeu, *Compt. rend.*, 1877, **84**, 177; Rousseau, *ibid.*, 1885, **101**, 167; 1886, **102**, 425; 1893, **116**, 1060.
[8] Risler, *Bull. Soc. chim.*, 1878, [2], **30**, 110; Rousseau, *Compt. rend.*, 1885, **101**, 167; Dufau, *Ann. Chim. Phys.*, 1897, [7], **12**, 257.
[9] Gorgeu, *Ann. Chim. Phys.*, 1862, [3], **66**, 153.
[10] Jezler, *Dingl. poly. J.*, 1875, **215**, 446; Lunge, *ibid.*, 1881, **242**, 371; Wiernik, *Zeitsch. angew. Chem.*, 1894, **7**, 257; Weldon, *Dingl. poly. J.*, 1873, **207**, 512; see *J. Chem. Soc.*, 1873, **26**, 949.
[11] Delaurier, *Chem. News*, 1869, **20**, 240.
[12] Auger and Billy, *Compt. rend.*, 1904, **138**, 500.

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Calcium Permanganate, $Ca(MnO_4)_2.5H_2O$, is obtained by the action of sodium permanganate on calcium chloride, forming a deliquescent crystalline mass.[1] It is decomposed by heat, giving manganate, manganese dioxide, and oxygen,[2] and is a powerful oxidising agent.[3]

The electrical conductivity of the solution has been studied by Franke.[4]

CALCIUM AND OXYGEN.

Calcium Suboxide, Ca_2O.—By heating together calcium oxide and magnesium at 850° C. in argon under reduced pressure a blackish fritted mass is obtained. It behaves similarly to calcium towards water, nitrogen, and hydrogen, and Guntz regarded it as calcium suboxide mixed with metallic magnesium.[5]

Calcium Oxide, CaO, also known as caustic lime or quicklime, may be formed by the direct combination of calcium and oxygen. The molecular heat of formation is about 152 Cal.[6] It can also be obtained by the calcination of the nitrate or the carbonate. For the preparation on the commercial scale the carbonate is used, and " lime-burning " is one of the oldest of chemical processes.

Among the chief sources of the carbonate is, first and foremost, limestone of varying degrees of purity. A limestone consisting of nearly pure carbonate gives a rich or " fat " lime. Limes containing aluminates and silicates are hydraulic limes (see Cement). Dolomitic limestone does not give a satisfactory product (see Cement), and is not used except for special purposes—for example, the lining of certain furnaces. Chalk may also be burnt, and in certain places in Holland and America sea-shells are used—for instance, in Baltimore, where the oyster-canning industry is carried on. Another source is the spent lime from paper-pulp mills, caustic-soda works, and beet-sugar factories.

Although the modern limekiln differs greatly in efficiency from the ancient one, and is a much more elaborate structure, the principle of the method of lime-burning has remained essentially the same. The carbonate is heated strongly to drive off the carbon dioxide, the usual working temperature being from 800° to 1000° C. The escape of the gas is facilitated by the presence of steam, which dilutes it and so reduces its partial pressure (see Calcium Carbonate). A lower temperature may thus be employed and an economy of fuel effected. In the older process the limestone was damped, but in the modern ones steam is injected into the kilns. In the simplest form of kiln, known as the flare kiln, the limestone in small pieces is supported over the fire on an arch made of larger lumps, the kiln itself being also constructed of limestone. The same form may be built of brick or stone and the inside lined with fireclay. The process is intermittent, the kiln being emptied and re-charged after each batch.

A more economical type is the continuous or running kiln. A long steel shaft, of a height three to four times the diameter, and lined with

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[1] Mitscherlich, *Pogg. Annalen*, 1832, **25**, 297.
[2] Rousseau, *Compt. rend.*, 1887, **104**, 786.
[3] McDermott, *J. Amer. Chem. Soc.*, 1913, **35**, 219.
[4] Franke, *Zeitsch. physikal. Chem.*, 1895, **16**, 475.
[5] Guntz, *Ann. Chim. Phys.*, 1907, [8], **10**, 448. See Barium Suboxide.
[6] Guntz and Bassett, *Compt. rend.*, 1905, **140**, 863; de Forcrand, *ibid.*, 1911, **152**, 27; Muthmann, Weiss, and Metzger (*Annalen*, 1907, **355**, 137) found 160 Cal., and Moissan (*Compt. rend.*, 1899, **128**, 384) 145 Cal.

firebrick, is necessary. Instead of steel, a reinforced-concrete shell has recently been recommended in America. The limestone and fuel may be fed in at the top in alternate layers. The fire is started at the bottom and more of the charge introduced at the top. If lime uncontaminated with ash is required, calcination must be effected by the hot gases from furnaces at the sides. As fuel in the latter case, wood, coal, oil, natural gas, or producer gas may be employed.

For the highest economy in fuel and labour, and for uniform and thorough burning, it is best to use a rotary kiln such as is adopted in cement-burning (see Cement). This method was first proposed in 1885,[1] but in spite of its advantages it is only in very recent times that it has met with much approval, because it produces lime in small pieces—from dust to pieces of 2 inches in diameter—and builders are prejudiced in favour of large lumps. Spent lime sludge may be fed into the rotary kiln whilst still wet, like cement slurry.[2]

Calcium oxide as ordinarily obtained is a white amorphous mass with a density which varies between 3·15 and 3·30 according to the temperature at which it has been prepared.[3] Hare stated that he had fused it in the oxyhydrogen flame, but probably the lime was not a very pure specimen.[4] It may be fused in the electric furnace giving on cooling a milky crystalline mass of density 3·4.[5] According to Day and Shepherd[6] the density of fused lime is 3·316 at 25° C. and the hardness 3–4. Moissan obtained crystals in the form of both cubes and needles.[5] Brugelmann obtained transparent cubical crystals of 2 mm. side and density 3·251, by slowly heating calcium nitrate with the addition of 0·25–0·6 per cent. of calcium hydroxide.[7]

The high melting-point of lime makes it difficult to determine its value with accuracy. Ruff and his collaborators[8] found that under reduced pressure it had not melted at 2450° C., but that it volatilised readily above 2000° C. Kanolt gave the melting-point as 2572° C.±3°.[9] The boiling-point of lime at 760 mm. is near 2850° C.[10] Considerable volatilisation takes place at 1500° C.[11] The latent heat of fusion is 490 small calories per gram.[12]

The molecular heat of calcium oxide at 2552° C. is 14·8 cal. or specific heat 0·242.[13] Laschtschenko studied the change of specific heat with temperature at lower temperatures.[14] He found the value 0·172 cal.

[1] Mathey, U.S.A. Patent, 330603 (1885).
[2] For details of recent improvements in the manufacture of lime, see Meade, *Chem. Met. Eng.*, 1920, 23, 841, 873, 929
[3] Brugelmann, *Zeitsch. anal. Chem.*, 1890, 29, 126; Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415; Schroeder, *Pogg. Annalen. Jubelbd.*, 1874, 452; Moissan, *Compt. rend.*, 1902, 134, 136.
[1] Hare, *Phil. Mag.*, 1802–1803, 14, 238, 298; *Ann. Chim. Phys.*, 1803, [1], 45, 113.
[5] Moissan, *Ann. Chim. Phys.*, 1902, [7], 26, 280; see also Jouve, *Compt. rend.*, 1901, 132, 1117.
[6] Day and Shepherd, *J. Amer. Chem. Soc.*, 1906, 28, 1089.
[7] Brugelmann, *Zeitsch. anorg. Chem.*, 1908, 59, 248.
[8] Ruff, Seiferheld, and Suda, *ibid.*, 1913. 82, 373; but in an earlier determination carried out in nitrogen Ruff and Goecke, *Zeitsch. angew. Chem.*, 1911, 24, 1459, found 1995° C.
[9] Kanolt, *Zeitsch. anorg. Chem.*, 1914, 85, 1.
[10] Ruff and Schmidt, *ibid.*, 1921, 117, 172.
[11] Thompson and Lombard, *Met. Chem. Eng.*, 1910, 8, 682.
[12] Washburn, *Trans. Amer. Ceram. Soc.*, 1917, 19, 195; see *J. Soc. Glass Tech.*, 1917, 1, Abs., 135.
[13] Wartenburg and Witzel, *Zeitsch. Elektrochem.*, 1919, 25, 209.
[14] Laschtschenko, *Compt. rend.*, 1908, 147, 58.

at 190° C., 0·181 at 376° to 400° C., 0·190 at 415° C., and thereafter a gradual increase to 0·193 between 590° and 680° C. He concluded that the fused lime had undergone transformation between 400° and 415° C., and that the heat of transformation was 0·280 Cal. per gram-molecule. In connection with this an observation of Moissan's might be mentioned.[1] He mounted some cubical crystals of lime in Canada balsam, and found, six months later, that they had broken into fragments which polarised light. He regarded this as evidence of dimorphism. Other indications have also been obtained of a transition point between 400° and 430° C., from a fine-grained porous form showing slight double refraction at low temperatures, to a cubic form at high temperatures.[2]

The reactivity of lime with non-metals and metals has been studied by Moissan.[1] Fluorine reacts with calcium oxide in the cold with the production of heat and light. Calcium fluoride is formed and oxygen given off. Other non-metals require the aid of heat. Chlorine at 300° C. will partially replace oxygen.[3] Sulphur, arsenic,[4] silicon, boron, and titanium also react. Carbon in the electric furnace forms first calcium carbide and carbon monoxide, and then, in the presence of excess of lime, the latter is reduced by the carbide producing metallic calcium. Many of the metals, even platinum, reduce lime to a greater or less extent at a sufficiently high temperature. Anhydrous calcium oxide will not react with the different acid gases, hydrochloric acid, carbon dioxide, sulphur dioxide, etc., in the cold, but on heating, reaction takes place.[5]

Vignon found that in the presence of lime, carbon reacted with steam at a lower temperature than when alone, producing hydrogen, methane, and ethylene, the proportion varying with the amount and rate of flow of the steam.[6] This probably has a bearing on the question of the formation of natural petroleum.

When heated in the oxyhydrogen flame, calcium oxide emits a brilliant white light, the well-known limelight. Under the influence of the cathode rays it gives an orange-yellow fluorescence.[7] Schmidt obtained a phosphorescent calcium oxide by grinding up with a small quantity of one of the following substances : sodium chloride, fluoride, and phosphate, calcium and magnesium fluoride, lithium phosphate, potassium hydrogen phosphate, and potassium borate, adding a nitric acid solution of bismuth, copper, manganese, or lead, and heating the whole to redness. It then phosphoresced after exposure to light. The position of brightest phosphorescence was at a shorter wave-length than in calcium sulphide and selenide.[8]

Calcium oxide dissolves in fused calcium chloride, one molecule of the oxide saturating seven of the chloride.[9]

[1] Moissan, loc. cit.
[2] Sosman, Hostetter, and Merwin, J. Wash. Acad. Sci., 1915, 5, 565.
[3] Veley, Trans. Chem. Soc., 1894, 65, 1.
[4] Soubeiran, Ann. Chim. Phys., 1830, [2], 43, 412
[5] Veley, Trans. Chem. Soc., 1893, 63, 821 ; Ber., 1896, 29, 577 ; Schumann, Annalen, 1877, 187, 286 ; Birnbaum and Wittich, Ber., 1880, 13, 651 ; Schulatschenko, Dingl. poly. J., 1872, 205, 345; Vogel, Jahresber., 1858, 126; Raoult, Compt. rend., 1881, 92, 189 ; Kolb, ibid., 1867, 64, 861.
[6] Vignon, Compt. rend., 1911, 152, 871.
[7] Crookes, Proc. Roy. Soc., 1881, 32, 206.
[8] Schmidt, Ann. Physik., 1920, [4], 63, 264.
[9] Arndt, Ber., 1907, 40, 427.

By heating the double carbonate of calcium and lithium an iso-morphous mixture of lime and lithia, crystallising in regular octahedra, can be obtained.[1]

A double oxide of calcium and lead is formed by dissolving lead oxide in boiling lime-water and allowing to crystallise.[2] The solution blackens wool.

Calcium Hydroxide, Ca(OH)$_2$.—Amorphous quicklime reacts with water with considerable rise of temperature and yields calcium hydroxide as a dry powder of rather more than twice its volume.[3] The process is known as "slaking." The molecular heat of solution of calcium oxide in water is 18·12 Cal.[4] The heat of solution of calcium hydroxide is 2·79 Cal., and therefore the heat of formation from calcium oxide and water is 15·33 Cal.

When the oxide has been strongly calcined the rate of reaction with water is very much less. Moissan obtained a sample of fused lime which was practically unaffected by twenty-four hours' immersion in water, although after seventy-two hours complete transformation into hydroxide had taken place. There is also a similar reluctance to react with dilute acids.[5] The velocity of reaction is further affected by the presence of foreign substances.[6] Hydrochloric and nitric acids, ammonium, calcium, and barium chlorides, acetic acid, lactic acid, and alcohol, behave as accelerators, and boric acid, caustic potash and soda, calcium chromate, potassium dichromate, aldehyde, glycerol, cane sugar, and grape sugar, as retarders. It is easy to understand the increase of rate of slaking in presence of an acid, which will tend to bring the lime into solution, and the retardation by an alkali, which tends to diminish the solubility; but the retarding action of sugar and glycerol, for example, which dissolve the lime, is not so readily explained. It might possibly be due to the fact that sugar and glycerol are highly hydrated in solution, thus diminishing considerably the concentration of free water in the liquid, and conceivably the rate of reaction also.

The presence of a large quantity of water also reduces the velocity of reaction, probably by keeping the temperature down.

The hydroxide formed by the slaking of lime is a white amorphous powder of density 2·078.[7] It is also obtained as an amorphous precipitate by the action of an alkali on a soluble calcium salt. Since the hydroxide dissolves in water with the evolution of heat, the solubility diminishes with increase of temperature.[8] By heating to 80° C. a solution saturated in the cold, the hydroxide crystallises out in small transparent hexagonal prisms of density 2·236.[9] The same crystals may also be obtained by evaporating the hydroxide solution under reduced pressure at 28°–30° C.[10]

By calcination the anhydrous calcium oxide may be again obtained.

[1] Lebeau, *Compt. rend.*, 1904, **138**, 1602 ; *Ann. Chim. Phys.*, 1905, [8], **6**, 433.
[2] Berthollet, *Ann. Chim. Phys.*, 1789, [1], **1**, 52.
[3] Cavazzi, *Gazzetta*, 1915, **45**, i., 529.
[4] de Forcrand, *Compt. rend.*, 1911, **152**, 27 ; see also Thomsen, *Ber.*, 1883, **16**, 2613.
[5] See also Gautier, *Compt. rend.*, 1899, **128**, 939.
[6] Rohland, *Zeitsch. anorg. Chem.*, 1899, **21**, 28.
[7] Filhol, *Ann. Chim. Phys.*, 1847, [3], **21**, 415.
[8] Tichborne, *Chem. News*, 1871, **24**, 199.
[9] Lamy, *Ann. Chim. Phys.*, 1878, [5], **14**, 145.
[10] Sehwanov, *Zeitsch. anorg. Chem.*, 1914, **85**, 329

The dissociation temperatures for different pressures have been determined.[1]

Temperature, °C	369	389	408	428	448	468	488	507	527	547
Mm mercury	9 2	17 4	31 5	55	92	149	234	355	526	760

Discordant values for the solubility of lime in water have been found. According to Lamy, the value depends on the temperature of preparation and source of the original calcium oxide, and on the method of slaking.[2] The following values have been obtained for the solubility of a lime prepared by igniting in a platinum dish, in a muffle, a very pure specimen of calcite[3] :—

Temperature, ° C	Grams of Water to dissolve 1 gram CaO.	Temperature, ° C.	Grams of Water to dissolve 1 gram CaO.
2	768·5	40	988 1
10	786 8	50	1083·0
15	804·3	60	1179 0
20	826 4	70	1274·8
25	868 7	80	1368 1
30	908·2		

The solubility is reduced by the presence of alkali hydroxide to a greater extent than is accounted for by electrolytic dissociation.[4] This has a bearing on the causticising of alkali carbonates by calcium hydroxide, this reaction being more complete in dilute than in concentrated solutions.[5] The presence of alkali chlorides increases the solubility, except in concentrated solutions.[6] In the case of ammonium chloride there is probably a complex salt formed, $2NH_4Cl.Ca(OH)_2$ or $Ca(NH_3)_2Cl_2.2H_2O$.[7]

Calcium hydroxide is also soluble in glycerol and in sugar solution.[8] The crystalline hydrate is less soluble in water and sugar solution than the amorphous form.[9]

The electrical conductivity of calcium hydroxide solutions has been determined.[10]

A transparent cryohydrate is obtained by freezing lime and water.

[1] Johnston, Zeitsch physikal. Chem., 1908, 62, 330 ; see also J. Amer. Chem Soc., 1908, 30, 1357.
[2] Lamy, loc. cit. ; Compt. rend., 1878, 86, 333 ; see also Maben, Pharm. J. and Trans., 1883, [3], 14, 505 ; Herzfeld, Zeitsch. Ver Rübenzuck. Ind., 1897, 817 ; Guthrie, J. Soc. Chem. Ind., 1901, 20, 223 ; d'Anselme, Bull. Soc. chim., 1903, [3], 30, 936.
[3] Moody and Leyson, Trans. Chem. Soc., 1908, 93, 1767; see also Haslam, Calingaert, and Taylor, J Amer. Chem. Soc., 1924, 46, 308.
[4] d'Anselme, loc. cit.
[5] d'Anselme, loc. cit. ; Bodlander, Zeitsch. angew. Chem., 1904, 17, 1519, and Lucas, ibid., 1905, 18, 1137 ; Le Blanc and Novotny, Zeitsch. anorg. Chem., 1906. 51, 181 ; Wegscheider, Annalen, 1907, 351, 87 ; see also Vol. II. of this series
[6] Cabot, J. Soc. Chem. Ind , 1897, 16, 417 ; Kernot, d'Agostino, and Pellegrino, Gazzetta, 1908, 38, i, 532 ; Kimúra, J. Chem. Ind. Tokyo, 1920, 23, 363, see Chem. Abs., 1920, 14, 2857.
[7] Berthelot, Bull. Soc. chim., 1875, [2], 24, 102 ; Ann. Chim. Phys., 1875, [5], 6, 446.
[8] Berthelot, Ann. Chim. Phys., 1856, [3], 46, 173.
[9] Seliwanov, loc. cit.
[10] Ostwald, J. prakt. Chem., 1886, [2], 33, 357.

On melting, this deposits elongated hexagonal plates, or small rhombic plates of the semihydrate, $2Ca(OH)_2.H_2O$, less soluble than the simple hydroxide and very unstable, passing into the amorphous form when only slightly heated.[1] Seliwanov considered that the amorphous hydroxide is a polymeride of $Ca(OH)_2$ containing not fewer than four atoms of calcium in the molecule.[1]

By slaking the oxide with excess of water at 60° C. and then cooling, a hydrate, $Ca(OH)_2.H_2O$, is obtained. This compound loses water even in the cold and is completely converted into $Ca(OH)_2$ at 70° C.[2] According to recent work, however, this hydrate does not exist.[3]

By continued addition of water to slaked lime, " milk of lime," a suspension of lime in water, is obtained. Kosmann supposes that a succession of hydrates is thus produced in the order, $Ca(OH)_2$, $HCa(OH)_3$, $H_2Ca(OH)_4$, $H_3Ca(OH)_5$, $H_4Ca(OH)_6$, $H_5Ca(OH)_7$, $H_6Ca(OH)_8$, and $H_7Ca(OH)_9$.[4] Kohlschutter and Walther, on studying the rate of sedimentation of calcium hydroxide in water, concluded that, in the formation of a true solution, an intermediate colloidal state is first obtained.[5] Two varieties of colloidal calcium hydroxide have been obtained from a calcined dolomite.[6]

Calcium oxide forms compounds with the alcohols which have been described as ethyl, propyl, amyl, butyl, and glyceryl alcoholates respectively.[7] Compounds with mannitol are also obtained.[8] According to de Forcrand these are addition compounds and not true alcoholates—for example, $4C_2H_5OH.3CaO$.[9] The latter is also formed by the action of absolute ethyl alcohol on calcium carbide in a sealed tube at 180° C.[10]

Calcium hydroxide forms several crystalline addition compounds with phenol, consisting of one molecule of hydroxide with 2, 4, and 6 molecules of phenol respectively. The first also forms a series of hydrates of composition $2Ca(OH)_2.4C_6H_5OH.(2n+1)H_2O$,[11] where " n " may have any value from 0 to 4. Thymol gives similar compounds. With nitro-phenols, however, nitro-phenates are formed owing to the greater acidity due to the presence of the nitro-group.[12]

Uses of Lime.—Calcium oxide may be used as a drying agent. It is more rapidly exhausted than fused calcium chloride, but, owing to its greater porosity, it is more efficient.[13]

Calcium oxide slaked with sodium hydroxide solution, and known as soda-lime, is used for various chemical operations in place of either constituent alone, being much more reactive than these. It is apparently an efficient absorbing agent for all manner of gases,[14] for example,

[1] Seliwanov, loc. cit.
[2] Herzfeld, loc. cit. ; Karez, Chem. Zeit., 1898, 22, 38.
[3] Haslam, Calingaert, and Taylor, loc. cit.
[4] Kosmann, Zeitsch. Elektrochem., 1920, 26, 175.
[5] Kohlschutter and Walther, ibid., 1919, 25, 159.
[6] von Glasenapp, Kolloid. Zeitsch., 1922, 31, 195.
[7] Destrem, Ann. Chim. Phys., 1882, [5], 27, 5.
[8] Ubaldini, ibid., 1859, [3], 57, 213.
[9] de Forcrand, Compt. rend., 1895, 120, 737.
[10] de Forcrand, ibid., 1894, 119, 1266.
[11] Seliwanov, J. Russ Phys. Chem. Soc., 1913, 45, 1535, see J. Chem. Soc., 1913, 104, Abs. ii., 322.
[12] Fritzsche, Annalen, 1859, 110, 150 ; Goddard, Trans. Chem. Soc., 1921, 119, 1161.
[13] Dover and Marsden, J. Amer. Chem. Soc., 1917, 39, 1609 ; see also Foote and Scholes, ibid., 1911, 33, 1309.
[14] Guareschi, Atti Acc. Torino, 1915-16, 51, 4, 59, 263, 372, 951, 1094 ; see J. Chem. Soc., 1916, 110, Abs. ii., 324, 325, 529, 562.

carbonyl chloride, sulphuretted hydrogen, antimony and arsenic hydrides, phosphorus vapour, cyanogen, cyanogen chloride, bromide, and iodide, and so on. Soda-lime becomes incandescent when a mixture of sulphuretted hydrogen and air is passed over it, owing to the vigorous reaction which it promotes between them. Guareschi suggests that it contains compounds such as $Ca(ONa)_2$, OHCaONa, or OH.CaO.CaONa.

Lime is very extensively employed in agriculture. Its value to the soil does not lie only in the neutralisation of the soil acidity. A considerable amount is adsorbed by the soil constituents either physically or chemically, and this adsorption appears to be followed by an increased adsorptive power of the soil for other bases—for example, potash and ammonia.[1] Lime also improves the physical condition of the soil and throws out of action aluminium and iron salts which might be injurious to the plants. There is apparently an optimum value for the ratio of calcium oxide to magnesium oxide in the soil.[2]

The most ancient use of lime is in the production of lime mortar (see Cement). Ordinary building-mortar is composed of lime and sand. In modern practice one volume of lime is used to three of aggregate. In old mortars the average appears to have been one to one. Experiment seems to show that the ratio one to two gives the strongest mortar.[3] The lime should be fairly rich and easily slaked, and the sand formed of sharp angular grains free from humus and clay. The lime is slaked before mixing the mortar, which is applied as a paste. The process of hardening consists essentially in the drying of the mortar. There is not sufficient water present to produce a crystalline calcium hydroxide. Where this is found, it results from accidental outside influences. There is, nevertheless, a tendency now to consider that the formation of crystalloids has a bearing on the hardening of mortar.[4]

The inert material, sand, prevents the formation of cracks in the mortar during drying, both by reduction of the relative shrinkage and by the action of capillary forces at the surface of separation between the sand and the lime. At the exposed surface of the mortar a second reaction takes place, which is not, however, considered to be essential to the hardening process. Carbon dioxide is absorbed, resulting in a network of closely interlaced crystals of calcium carbonate, which do not extend beyond the outer layer, as can be seen by examining the mortar from old Roman buildings. If this has been undisturbed it still consists mainly of calcium hydroxide. It was formerly supposed that the hardening of mortar is in part due to the gradual formation of calcium silicate, but this view is now discredited. Silicates are found in old mortars, but there is no reason to suppose that they were not present in the original lime.

It is not advisable to use dolomitic limestone for the manufacture of lime for mortar. The hydration of the magnesia only takes place slowly, and may occur after the mortar is in position, and by expansion cause disintegration.[5]

[1] Hager, *J. f. Landwirtschaft*, 1917, 65, 245, see *J. Chem. Soc.*, 1918, Abs. i., 114, 247; Russell, *App. Chem. Reports*, 1920, 5, 379.

[2] Pfeiffer and Rippel, *J. f. Landwirtschaft*, 1920, 68, 4, see *Chem. Abs.*, 1920, 14, 3440.

[3] Dibdin, *Trans. Faraday Soc.*, 1919, 14, 31.

[4] Dibdin, *loc. cit.*; von Glasenapp, *Chem. Zeit.*, 1914, 38, 588.

[5] For further information see Rohland, Abegg's *Handbuch d. anorg. Chem.* (S. Hirzel), Leipzig, 1905, ii., 2, Mörtel, p. 180; Desch, *The Chemistry and Testing of Cement* (E. Arnold), 1911, ch. ii.; Dancaster, *Limes and Cements* (Crosby Lockwood & Son), 1916.

Lime is employed in the purification of sugar through the precipitation of impurities and the intermediate formation of mono-, di-, and tri-calcium saccharate, although the use of strontia has superseded that of lime in the treatment of molasses.[1]

In the purification of coal-gas, carbon dioxide, sulphuretted hydrogen, and carbon bisulphide are removed by lime. There is some doubt as to the nature of the reaction with the carbon bisulphide. A certain amount of oxygen is necessary, but too much is as harmful as too little. Veley[2] regarded calcium hydroxyhydrosulphide, $Ca(OH)(SH)$, as the active compound, but Lewes[3] suggested that the real agent is calcium disulphide, CaS_2, formed from the hydrosulphide by oxidation, because this would readily combine with carbon bisulphide to form a perthiocarbonate.[4] This explains the necessity for oxygen. Excess oxygen carries the oxidation further to thiosulphate, and so prevents the reaction. An observation by Walker[5] may have a bearing on the question of the absorption of carbon bisulphide. If the latter be shaken with milk of lime, orange crystals are obtained. Their composition corresponds to the formula $CaCS_3.2Ca(OH)_2.6H_2O$.

Lime is employed in the leather industry on account of its depilatory power.[6] It is also used for the causticising of alkalies.[7] Lime acts as a clarifying agent for sewage by coagulating the colloids, and in pharmacy lime-water mixed with linseed oil yields the so-called carron oil for the treatment of burns.

Calcium Peroxide, CaO_2.—Calcium peroxide was first obtained in the hydrated form, $CaO_2.8H_2O$, by the action of hydrogen peroxide on lime-water.[8] The anhydrous compound may be prepared by gently heating this octahydrate,[9] or by drying over phosphorus pentoxide in a desiccator. Dissociation begins, however, before dehydration is complete.[10] By precipitation from very concentrated solutions near 0° C., and even from very dilute solutions above 40° C., the anhydrous peroxide may be obtained without the intermediate formation of the hydrate.[11]

Jaubert took out patents for the production of calcium peroxide, or " Bicalzit," on a commercial scale by compressing a mixture of 78 parts of sodium peroxide with 74 parts of dry hydrated lime into cylinders of 500 grams each. These, by subsequent treatment with iced water, gave a precipitate of calcium peroxide which was washed and dried, first at ordinary temperatures, and finally at 100° C.[12]

According to Vaubel,[13] when dry calcium hydroxide is exposed to

[1] Heriot, *The Manufacture of Sugar from the Cane and Beet* (Longmans, Green & Co.), 1920 (Monographs on Industrial Chemistry); Martin, *Industrial Chemistry, Organic* (Crosby Lockwood & Son), Part I., 1920, p. 150; Thorpe, *Dictionary of Applied Chemistry* (Longmans, Green & Co.), 1913, vol. v., p. 211.

[2] Veley, *Trans. Chem. Soc.*, 1885, 47, 478.

[3] Thorpe, *Dictionary of Applied Chemistry* (Longmans, Green & Co.), 1922, vol. iii., p. 337.

[4] Gélis, *Compt. rend.*, 1875, 81, 282.

[5] Walker, *Chem. News*, 1874, 30, 28.

[6] Thompson, *App. Chem. Reports*, 1920, 5, 362.

[7] See Vol. II. of this series.

[8] Thénard, *Ann. Chim. Phys.*, 1818, [2], 8, 306.

[9] Schöne, *Ber.*, 1873, 6, 1172; *Annalen*, 1878, 192, 257.

[10] de Forcrand, *Compt. rend.*, 1900, 130, 1388.

[11] Riesenfeld and Nottebohm, *Zeitsch. anorg. Chem.*, 1914, 89, 405.

[12] Jaubert, English Patent, 17460 (1900); German Patents, 128617, 132706 (1902).

[13] Vaubel, *Zeitsch. angew. Chem.*, 1912, 25, 2300; *J. prakt. Chem.*, 1913, [2], 88, 61.

the air for some days, a small amount of peroxide is formed. To this he ascribed the corrosive action of lime mortar on lead, and the disinfecting power of slaked lime. Ditz contradicts this.[1]

The molecular heat of formation of calcium peroxide from the oxide and oxygen is 5·43 Cal.,[2] or from its elements, 157·37 Cal.[3] When dry it may be heated up to 200° C. without decomposition. Riesenfeld and Nottebohm studied the variation of dissociation pressure with temperature.[4] They observed no appreciable decomposition below 220° C. Up to 273° C. the decomposition was slow, but above that temperature it became rapid. At 255° C. the pressure was more than 190 atmospheres. They concluded that the production of calcium peroxide by the direct action of oxygen on lime would require pressures unattainable in practice.

Calcium peroxide is very little soluble in water, which decomposes it, and insoluble in alcohol and ether. Complete decomposition in aqueous solution is only effected after boiling for several hours.[5]

Commercial calcium peroxide without water of crystallisation contains 60 per cent. peroxide, the rest being lime.[5]

Calcium Peroxide Octahydrate, $CaO_2.8H_2O$. — The production of this compound by Thénard has already been mentioned. It is a white crystalline body, and may also be obtained by the action of sodium peroxide on a solution of a calcium salt, or by pouring an excess of limewater into a solution of sodium peroxide slightly acidified with nitric acid.[6] De Forcrand stated that the precipitated octahydrate always contains lime unless more than two molecules of hydrogen peroxide to one of lime are present. The molecular heat of formation of the octahydrate is 24·666 Cal.[7]

Calcium Peroxide Dihydrate, $CaO_2.2H_2O$. — De Forcrand obtained the dihydrate by precipitation with hydrogen peroxide above 20° C., but considered that its formula should be $Ca(OH)_2.H_2O_2$.[7] According to von Foregger and Philipp,[8] the dihydrate is formed when commercial calcium peroxide is added to water, but it then undergoes intramolecular change,

$$CaO_2.2H_2O = Ca(OH)_2.H_2O_2.$$
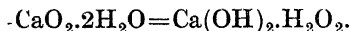
De Forcrand gave 6·815 Cal. as the molecular heat of formation from the anhydrous peroxide.

Uses of Calcium Peroxide.—Calcium peroxide may be employed with sulphuric acid for bleaching cotton-seed oil. Von Foregger and Philipp suggested that it might prove a useful sterilising agent for milk. Freyssing and Roche proposed the use of " Bicalzit " to sterilise drinking water. The action is not very rapid, but is complete after two or three hours. According to Hetsch, under certain conditions it acts more

[1] Ditz, *J. prakt. Chem.*, 1913, [2], 87, 208 ; 88, 443 ; *Zeitsch. angew. Chem.*, 1913, 26, 596.

[2] de Forcrand, *loc. cit.*

[3] de Forcrand, *Ann. Chim. Phys.*, 1908, [8], 15, 433.

[4] Riesenfeld and Nottebohm, *Zeitsch. anorg. Chem.*, 1915, 90, 371 ; see also Fischer and Ploetze, *ibid.*, 1912, 75, 10.

[5] von Foregger and Philipp, *J. Soc. Chem. Ind.*, 1906, 25, 298.

[6] Conroy, *J. Chem. Soc.*, 1873, 26, 808 ; *Chem. News*, 1873, 27, 29.

[7] de Forcrand, *Compt. rend.*, 1900, 130, 1308.

[8] von Foregger and Philipp, *loc. cit.* See also Riesenfeld and Nottebohm, *loc. cit.*

energetically than hydrogen peroxide, and 0·5 grm. per litre is fatal to typhoid bacilli.[1]

Peroxyhydrates of Calcium.—By the action of concentrated hydrogen peroxide on calcium peroxide octahydrate at low temperatures, Riesenfeld and Nottebohm obtained a compound which they described as a diperoxyhydrate, $CaO_2.2H_2O_2$.[2] By stopping the action after a shorter time a monoperoxyhydrate, $CaO_2.H_2O_2$, is obtained as a heavy, faintly yellow powder.[3]

Calcium Tetroxide, CaO_4.—By heating the octahydrate at a low temperature a yellow powder is obtained. On raising the temperature still further it becomes white again. Riesenfeld and Nottebohm regarded the yellow as a labile form of calcium peroxide, and the white as the stable form. Traube and Schulze, however, showed that the yellow compound is probably calcium tetroxide, the composition of which, they considered, is best expressed by the formula $CaO_2.O_2$, comparable with the polysulphides of calcium.[3] It may be obtained by simply filtering and drying the monoperoxyhydrate, or better still, by heating the peroxide octahydrate with 30 per cent. hydrogen peroxide on the water-bath until evolution of oxygen ceases. It can also be prepared by digesting finely powdered calcium carbonate with hydrogen peroxide, or by merely heating calcium peroxide octahydrate with water at 100° C. When the octahydrate is dehydrated *in vacuo* it takes on a slightly yellow colour, probably indicating the formation of a little tetroxide. The latter cannot be formed by treating anhydrous calcium peroxide with aqueous hydrogen peroxide, and this leads to the conclusion that the octahydrate is necessary for its production, because only the di-hydrate is obtained by the action of water on the anhydrous peroxide. When ultra-violet light acts upon the peroxide moistened with hydrogen peroxide the tetroxide is rapidly formed. It does not appear to be obtained by means of any other oxidising agent.

The tetroxide forms a yellow powder insoluble in water, alcohol, and ether. When dry it is a comparatively stable substance and can be heated to 130° C. without change. At 270°–290° C. the peroxide is formed. On treatment with acid there is effervescence, due to the evolution of half the total oxygen in an "inactive" form—that is, it has not the oxidising properties of nascent oxygen—and hydrogen peroxide remains in solution, hence the formula $CaO_2.O_2$, comparable with those of the alkali tetroxides.[4]

CALCIUM AND SULPHUR.

Calcium Monosulphide, CaS.—Calcium sulphide has been found in the natural state in a meteorite fallen in India.[5] It may be prepared by any of the following methods :—

1. The action of sulphuretted hydrogen on calcium carbonate[6] or sulphate[7] at red heat.

[1] S. and E. K. Rideal, *Water Supplies* (Crosby Lockwood & Son), 1914.
[2] Riesenfeld and Nottebohm, *Zeitsch. anorg. Chem.*, 1914, **89**, 405.
[3] Traube and Schulze, *Ber.*, 1921, **54B**, 1626.
[4] Traube, *ibid.*, 1916, **49**, 1670.
[5] Flight and Maskelyne, *ibid.*, 1870, **3**, 39.
[6] Sabatier, *Ann. Chim. Phys.*, 1881, [5], **22**, 5.
[7] Mourlot, *ibid.*, 1899, [7] **17**, 510.

2. The action of sulphuretted hydrogen on calcium hydroxide.[1] The reaction begins at 60° C. Anhydrous calcium oxide does not absorb the dry gas at low temperatures, but at red heat gives the sulphide.[2]

3. The reduction of calcium sulphate by carbon,[3, 4] moist hydrogen,[4] water gas,[4] carbon monoxide,[5] or sulphur.[6] This method is the most convenient technically, especially the reduction by carbon.

4. The action of sulphur on calcium carbonate,[6] and on anhydrous calcium oxide at red heat in a current of hydrogen.[7]

5. The action of sodium sulphide on calcium carbonate at red heat.[8]

6. The action of carbon bisulphide on quicklime at high temperatures.[9] The last method produces the purest sulphide.

Pure calcium sulphide is white, but the commercial product is generally coloured yellow, or yellowish red, by impurities in the original materials. It is usually obtained as an amorphous powder of density 2·25, but by fusion in the electric furnace, or by preparation through reduction of the sulphate by carbon in the electric furnace, brilliant cubical crystals of density 2·8 at 15° C. are produced.[10]

The molecular heat of formation from the metal and solid sulphur is 94·3 Cal.,[11] from gaseous sulphur 114·82 Cal.[12]

Calcium sulphide is stable in air, and more readily fusible at high temperatures than the corresponding strontium and barium compounds.

It is only slightly soluble in water, 0·212 grm. dissolving in one litre at 20° C.,[13] but it is readily hydrolysed with the formation of the more soluble products calcium hydroxide and hydrosulphide.[14] The crystalline sulphide is more readily attacked than the amorphous compound. The molecular heat of solution is 6·3 Cal.[15] The solubility is greatly increased by the presence of sulphuretted hydrogen through the formation of hydrosulphide. At 20° C., and under a pressure of gas of 760 mm., the solubility calculated as sulphide is 206·5 grm. per litre.[16] This affords a means of purifying calcium sulphide by extracting the crude material with sulphuretted hydrogen solution under pressure in absence of air, and then precipitating pure calcium sulphide by removing the gas from the solution at low pressures.

Calcium sulphide is a by-product of the Le Blanc process, and is treated for the recovery of sulphur.[17]

[1] Veley, Trans. Chem. Soc., 1885, 47, 478; Wright, J. Soc. Chem. Ind., 1883, 2, 122.

[2] Berzelius, Schweigger's J., 1822, 34, 12.

[3] Berthier, Ann. Chim. Phys., 1823, [2], 22, 225; 24, 271; Edmond Becquerel, ibid., 1848, [3], 22, 244.

[4] Unger, Annalen, 1848, 67, 78

[5] Stammer, Pogg. Annalen, 1851, 82, 135; Hofmann and Mostowitsch, Bull. Amer. Inst. Mining Eng., 1910, 917; see Chem. Zentr., 1911, i, 1737.

[6] Sestini, Ber., 1874, 7, 1295.

[7] Forster, Pogg. Annalen, 1868, 133, 258.

[8] Scheurer-Kestner, Ann. Chim. Phys., 1864, [4], 1, 412; Dubrunfaut, Bull. Soc. chim., 1864, [2], 1, 346.

[9] Schöne, Pogg. Annalen, 1861, 112, 199.

[10] Mourlot, loc. cit.; Compt. rend., 1898, 127, 408.

[11] Perkin and Pratt, Trans. Faraday Soc., 1908, 3, 179; Sabatier found 92 Cal., Ann. Chim. Phys., 1881, [5], 22, 5.

[12] de Forcrand, Ann. Chim. Phys., 1911, [8], 24, 272.

[13] Riesenfeld and Feld, Zeitsch. anorg. Chem., 1921, 116, 213.

[14] Pelouze, Ann. Chim. Phys., 1866, [4], 7, 172; Béchamp, ibid., 1869, [4], 16, 202; Clermont and Frommel, ibid., 1879, [5], 18, 189; Rose, Pogg. Annalen, 1842, 55, 415.

[15] de Forcrand, loc. cit.

[16] Riesenfeld and Feld, loc. cit.

[17] See Vol. II.

Phosphorescent Calcium Sulphide.—Calcium sulphide as usually prepared—that is, containing a certain amount of impurity—phosphoresces after exposure to a bright light or some other exciting agent, such as cathode rays. It was used in very early times in Bacchanalian rites, and later became known as Canton's phosphorus. The pure compound does not possess this property, which is apparently associated with the presence of minute quantities of certain heavy metals, notably bismuth, copper, manganese, nickel, vanadium, tungsten, molybdenum, and the rare earths. The nature of the impurity affects the colour of the phosphorescence, and the quantity influences the intensity, an optimum value being found.[1] The presence of a little alkali sulphate or carbonate is apparently also necessary.[2]

According to Waentig,[3] phosphorescence is conditioned by the presence of the heavy metal, or phosphorogen, in the form of a solid solution, the intensity increasing so long as the solution is homogeneous. This would explain the existence of a maximum value with increasing quantity of the heavy metal. The solubility is very small, but increases with temperature, so that the phosphorescent sulphides are supersaturated solutions—temperature, duration of heating, and rate of cooling being important factors in their preparation. The presence of a fusible alkali salt is favourable, because it aids the solution of the phosphorogen and hinders its separation during cooling.

Vanino and Zumbusch[4] made a careful study of the factors influencing the phosphorescing power of calcium sulphide or Bolognian stones. They drew the following conclusions : The most favourable quantity of bismuth for example, as phosphorogen, is of the order of 0·000135 grm. per grm. of sulphide. An alkali salt of low melting-point is better than one of high, and it is possible to use too large a quantity, 2 per cent. of lithium carbonate, for instance, is better than 12 per cent. The physical structure of the lime used for preparing the sulphide (by heating with sulphur) influences the final product. For example, the oxide from the hydroxide or carbonate is better than that from the nitrate—it probably influences the amount of polysulphide. A mixture of the alkaline earths gives a more intense phosphorescence than any one alone. The proportion of sulphur may vary between 12 and 33 per cent., but with more the luminosity is considerably diminished. The texture of the sulphide is important, if hard and stony it is non-luminous. There is no connection between colour photo-sensitiveness and phosphorescing power.[5] Finally, the presence of a reducing agent, for example 4 per cent. starch, is advantageous, although larger quantities may completely destroy the phosphorescence.

Mourelo[6] observed that some specimens of calcium sulphide change colour under the influence of light and that, although the phosphorogen is also the phototrope, this phototropic property is apparently in-

[1] Verneuil, *Compt. rend.*, 1886, **103**, 600 ; 1887, **104**, 501 ; Becquerel, *Ann. Chim. Phys.*, 1848, [3]. **22**, 244 ; *Compt. rend.*, 1887, **104**, 551 ; Bruninghaus, *ibid.*, 1907, **144**, 839, 1040; Kowalski and Garnier, *ibid.*, 1907, **144**, 836 ; Donau, *Monatsh.*, 1913, **34**, 949.
[2] Becquerel, *Compt. rend.*, 1888, **107**, 892 ; de Visser, *Rec. Trav. chim.*, 1903, **22**, 133 ; Breteau expresses the contrary view, *Compt. rend.*, 1915, **161**, 732.
[3] Waentig, *Zeitsch. physikal. Chem.*, 1903, **44**, 499 ; 1905, **51**, 435.
[4] Vanino and Zumbusch, *J. prakt. Chem.*, 1909, [2], **80**, 69 ; 1910, [2], **82**, 193.
[5] See also Mourelo.
[6] Mourelo, *Arch. Sci. phys. nat.*, 1908, [4], **25**, 15, see *J. Chem. Soc.*, 1908, **94**, Abs. ii., 140 ; *Compt. rend.*, 1914, **158**, 122 ; 1915, **161**, 172.

dependent of the phosphorescing power of the compound. The change in colour is confined to the surface exposed to light, and no regularity can be observed between the colour assumed and the composition. The intensity of phototropy increases as the percentage of phosphorogen diminishes from 0·1 to 0·0001, but beyond this it decreases and soon disappears.

Lenard and Saeland [1] regard photo-electric action as intimately connected with the phosphorescence of sulphides and as localised in certain centres which are also centres of light emission. Excitation by light or cathode rays consists in the loss of an electron from an atom of the foreign metal, and the resulting phosphorescence is due to the recombination of the metal with electrons. In this connection Perrin's view is interesting.[2] He considers that chemical reaction takes place under the influence of the exciting rays, and that this is reversed in the dark with the emission of energy as phosphorescent radiation.

The electrical conductivity of calcium sulphide is affected by exposure to light, and there appears to be a connection between conductivity and phosphorescence.[3]

Observations on phosphorescence spectra at temperatures down to −259° C. show that the bands become sharper and narrower as the temperature falls, and that different bands belong to different temperature ranges.[4]

Calcium Hydrosulphide, $Ca(SH)_2$, is formed in solution by saturating lime-water with sulphuretted hydrogen,[5] by the action of water or sulphuretted hydrogen solution under pressure on the sulphide,[6] or by the action of sulphuretted hydrogen on a suspension of calcium carbonate in water.[7] By treating milk of lime containing 1 part of hydrate to 4 of water with sulphuretted hydrogen, and cooling to a low temperature in the same gas, colourless prismatic crystals of the hexahydrate, $Ca(SH)_2.6H_2O$, are obtained.[8] They are very soluble in water and alcohol, 4 parts by weight of the crystals dissolving in 1 of water at ordinary temperatures, and the compound is readily hydrolysed, only the hydroxide being left if the solution is dilute. Heat facilitates the reaction.[9] On warming, the crystals of the hydrosulphide melt with decomposition into sulphuretted hydrogen and calcium monosulphide.

The depilatory properties of calcium hydrosulphide have long been known.

Polysulphides of Calcium.—If calcium sulphide and sulphur are boiled together with water they dissolve, forming yellow-red solutions

[1] Lenard and Saeland, *Ann. Physik*, 1909, [4], **28**, 476; see also Göggel, *ibid.*, 1922, [4], **67**, 301.

[2] Perrin, *Ann. Physique*, 1919, [9], **11**, 57.

[3] Vaillant, *Compt. rend.*, 1912. **154**, 867; 1920, **171**, 713, 1380.

[4] Lenard, Kamerlingh Onnes, and Pauli, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 157.

Further literature: Lecoq de Boisbaudran, *Compt. rend.*, 1886–9, **103–109**, several papers; Lenard and Klatt, *Ann. Physik*, 1904, [4], **15**, 225, 633; Bachem, *ibid.*, 1912, [4], **38**, 697; Baerwald, *ibid.*, 1912, [4], **39**, 849; Vanino and Gans, *J. prakt. Chem.*, 1905, [2], **71**, 196.

[5] Boettger, *Annalen*, 1839, **29**, 79; 1840, **33**, 344; Pelouze, *Compt. rend.*, 1866, **62**, 108; Veley, *Trans. Chem. Soc.*, 1885, **47**, 478.

[6] Kraushaar, *Dingl. poly. J.*, 1877, **226**, 412; *Trans. Chem. Soc.*, 1878, **34**, 171.

[7] Béchamp, *Ann. Chim. Phys.*, 1869, [4], **16**, 202.

[8] Divers and Shimidzu, *Trans. Chem. Soc.*, 1884, **45**, 270.

[9] Miller and Opl, *Dingl. poly. J.*, 1884, **253**, 350.

which are considered to contain CaS_5, CaS_4, and probably CaS_2.[1] Polysulphides, along with calcium thiosulphate, are also formed by boiling together lime and sulphur in water for the production of a lime-sulphur spray as an insecticide for animals and plants, especially in the Pacific States.[2]

Auld concluded, from experiments on the action of dilute acids, that polysulphides of sulphur content at least as high as CaS_7 were formed, and suggested that the constitution is represented by the formula

$$Ca\diagdown_S^S \diagup S=S=S= \ldots,$$ the sulphur atoms in the chain becoming

progressively more loosely attached.[3]

Barbieri fixed the polysulphides with hexamethylenetetramine and then determined their composition. He obtained the compounds $CaS_5.10H_2O.2C_6H_{12}N_4$ and $CaS_4.10H_2O.2C_6H_{12}N_4$, and concluded that CaS_5 is formed by saturating calcium hydrosulphide with sulphur, and CaS_4 by boiling sulphur with lime.[4]

Solutions of polysulphides readily hydrolyse, producing calcium hydroxide, sulphur, and sulphuretted hydrogen.

A compound containing polysulphides, and known as "liver of sulphur," is obtained by calcining together equal weights of calcium oxide and sulphur.

Calcium Hydroxyhydrosulphide, $Ca(SH)(OH).3H_2O$, is obtained by the action of a little water or lime on the hydrosulphide,[5] or on the sulphide, or of the sulphide or sulphuretted hydrogen on calcium hydroxide as in the purification of coal-gas. It is obtained in four-sided prisms or fine needles which lose hydrogen sulphide in the air, becoming yellow and opaque. It readily dissolves in water, forming the hydrate, and it absorbs carbon bisulphide with the production of a basic thiocarbonate, $2Ca(OH)_2.CaCS_3.10H_2O$.

Oxysulphides of Calcium. — A mixture of calcium hydroxide and sulphide, regarded by Folkard[6] as a molecular compound, $4Ca(OH)_2.3H_2S$, is obtained by passing a dry mixture of hydrogen and sulphuretted hydrogen over calcium hydroxide. At 100° C. the composition may be expressed by the formula $2Ca(OH)_2.2Ca(OH)(SH)$, and at red heat in an inert gas, $2CaO.2CaS.H_2O$. By further heating, calcium sulphate may be obtained. Orange-yellow prismatic crystals, to which several different formulæ have been ascribed, $CaO.CaS_2.7H_2O$, $3CaO.CaS_4.12H_2O$, $2CaO.CaS_3.10$ or $11H_2O$, $CaS_3.3CaO.14$ or $15H_2O$, $CaS_4.4CaO.18H_2O$, and $CaS_5.5CaO.20H_2O$, can be obtained by boiling together calcium hydroxide, sulphur, and water,[7] by treating a fused

[1] Schöne, *Pogg. Annalen*, 1862, **117**, 58

[2] Divers and Shimidzu, *loc. cit.*; Divers, *Trans Chem. Soc.*, 1884, **45**, 696; Haywood, *J. Amer. Chem. Soc.*, 1905, **27**, 244; Thatcher, *ibid.*, 1908, **30**, 63; Bradley and Tartar, *J. Ind. Eng. Chem.*, 1910, **2**, 271; van Slyke, Hedges, and Bosworth, *J. Soc. Chem. Ind.*, 1910, **29**, 589; Tartar, *J. Amer. Chem. Soc.*, 1913, **35**, 1741; 1914, **36**, 495; *J. Ind Eng. Chem.*, 1914, **6**, 488; Ramsay, *J. Agri Sci.*, 1914, **6**, 194, 476; Bodnar, *Chem. Zeit.*, 1915, **39**, 715; Auld, *Trans. Chem. Soc.*, 1915, **107**, 480.

[3] Auld, *loc. cit.*

[4] Barbieri, *Atti R. Accad. Lincei*, 1914, [5], **23**, ii., 8, see *Chem. Zentr.*, 1914, ii., 816.

[5] Divers and Shimidzu, *loc. cit.*

[6] Folkard, *Chem. News*, 1884, **49**, 258.

[7] Herschell, *Ann. Chim. Phys.*, 1820, [2], **14**, 353, from *Edinburgh Phil. J.*, i., 8, 396; ii., 154; Schöne, *Pogg. Annalen*, 1862, **117**, 77; Geuther, *Annalen*, 1884, **224**, 178.

mixture of lime and sulphur with hydrochloric or acetic acid,[1] or by evaporating a solution of the hydrosulphide.[2] The crystals are monoclinic,[3] gradually become colourless on exposure to air, and are decomposed by water but not by alcohol.

Calcium Thiosulphate, CaS_2O_3, is prepared by boiling lime-water with sulphur, saturating the liquid at the same time with sulphur dioxide, and evaporating below 60° C.[4] It may also be obtained by the reduction of calcium sulphate by sulphur,[5] by the action of sulphur on calcium sulphite and water between 30° and 40° C.,[6] or by mixing concentrated solutions of sodium thiosulphate and calcium chloride, removing by filtration the sodium chloride first formed, concentrating at about 50° C., and allowing to crystallise.[7]

Calcium thiosulphate is also formed when lime which has been used for coal-gas purification is exposed to the air,[8] and it is a by-product of the Le Blanc process.

It forms colourless, six-sided, triclinic crystals of composition $CaS_2O_3.6H_2O$,[9] which effloresce *in vacuo* or in dry air above 40° C. The density is 1·872.[10] The solubility at 9° C. is 29·4 grm. of anhydrous salt in 100 grm. of water, and at 25° C. 34·7 grm. In each case the solution is dissociated electrolytically to the extent of about 0·6 per cent.[11]

On keeping, calcium thiosulphate gradually decomposes into sulphur, sulphide, and sulphate.

A triple salt with sodium nitrate and sodium thiosulphate, of composition $NaNO_3.CaS_2O_3.Na_2S_2O_3.11H_2O$, has been obtained.[11]

Calcium Hyposulphite, CaS_2O_4, may be obtained by gently warming calcium hydride with sulphur dioxide.[12] The reaction is slow under ordinary pressure and can only be completed above 900 mm. By the electrolysis of a solution of calcium bisulphite under suitable conditions calcium hyposulphite crystallises out in silky needles, a current efficiency of 60–70 per cent. being obtained.[13] The dry salt is unstable. The solution of the salt has strong reducing properties. With hydrochloric acid it becomes yellow and deposits sulphur.

Calcium Sulphite, $CaSO_3$, may be precipitated by the action of sulphur dioxide on either calcium hydroxide [14] or calcium carbonate [15] in water. It crystallises in colourless hexagonal prisms,[16] forming $CaSO_3.2H_2O$. The whole of the water may be removed by heating to

[1] Bucholz and Brandes, *Schweigger's J.*, 1818, 22, 43.
[2] Rose, *Pogg. Annalen*, 1842, 55, 433.
[3] Groth, *ibid.*, 1868, 135, 658.
[4] Herschell, *loc. cit.*
[5] Kopp, *Bull. Soc. Mulhausen*, 1857, 28, 436.
[6] Divers, *Trans. Chem. Soc.*, 1884, 45, 696.
[7] Kessler, *Annalen*, 1848, 68, 231.
[8] Graham, *Phil. Mag.*, 1845, [3], 27, 121.
[9] Zepharowich, *Jahresber.*, 1862, 131.
[10] Clarke, *Constants of Nature*, Part I. (Macmillan & Co.), 1888.
[11] Kremann and Rodemund, *Monatsh.*, 1914, 35, 1061.
[12] Moissan, *Compt. rend.*, 1902, 135, 647.
[13] Frank, *Zeitsch. Elektrochem.*, 1904, 10, 450; but see Elbs and Becker, *ibid.*, 1904, 10, 361.
[14] Muspratt, *Annalen*, 1844, 50, 259.
[15] Fourcroy and Vauquelin, *Ann. Chim.*, 1797, [1], 24, 229; Berthollet, *ibid.*, 1789, [1], 2, 54; Rammelsberg, *Pogg. Annalen*, 1846, 67, 249; Röhrig, *J. prakt. Chem.*, 1888, [2], 37, 217.
[16] Muspratt, *loc. cit.*

150° C. in a current of pure hydrogen.[1] By heating the crystallised salt to 80° C., $2CaSO_3.H_2O$ is obtained.[2] On exposure to air it oxidises to calcium sulphate, and on heating above 450° C. it breaks up into calcium sulphide and sulphate.[3]

Calcium sulphite is only slightly soluble in water, and increase in temperature decreases the solubility. There seems to be some doubt, however, as to the actual values.[4] The following figures have been given[5] :—

Temperature, ° C.	Percentage Solubility of $CaSO_3.2H_2O$ in Water
30	0·064
60	0·061
100	0·011

The presence of sugar increases the solubility.

Calcium Bisulphite, $Ca(HSO_3)_2$.—Calcium sulphite is soluble in an aqueous solution of sulphur dioxide, probably on account of the formation of an acid sulphite, $Ca(HSO_3)_2$. Elbs and Becker found the maximum solubility to be 9·3 grm. per litre,[6] but according to Frank[7] much more concentrated solutions can be obtained. The salt has not been obtained in the solid state.

A solution of calcium bisulphite, prepared commercially by the action of sulphur dioxide on milk of lime, is used as an antiseptic in the brewing industry.[8] It is also employed for bleaching cellulose in the manufacture of paper.[9]

Basic Calcium Sulphite, $3CaO.5SO_2$, is obtained by heating calcium oxide with sulphur dioxide above 400° C.[10]

Calcium Dithionate, CaS_2O_6, is obtained by the action of milk of lime on manganese dithionate, or by neutralising dithionic acid with calcium hydroxide. After concentration of the filtrate, colourless rhombohedric crystals containing 4 molecules of water of crystallisation are obtained.[11] The crystals are stable in air and have a density of 2·18.[12] They rotate the plane of polarisation of light.[13] One part of dithionate is soluble in 2·46 parts of water at 19° C. and 0·8 part at 100° C., but it is insoluble in alcohol.

[1] Carius, *Annalen*, 1858, 106, 328.

[2] Röhrig, *loc. cit.*

[3] Rammelsberg, *loc. cit.*

[4] Weisberg, *Bull. Soc. chim.*, 1896, [3], 15, 1247; Robart, *Bull. Assoc. chim. Sucr. Dist.*, 1913, 31, 108, see *J. Chem. Soc.*, 1913, 104, Abs. ii., 959; van der Linden, *Chem. Zentr.*, 1917, i., 366.

[5] Heriot, *Manufacture of Sugar from Cane and Beet* (Monographs on Industrial Chemistry) (Longmans, Green & Co.), 1920, p. 185.

[6] Elbs and Becker, *Zeitsch. Elektrochem.*, 1904, 10, 361.

[7] Frank, *ibid.*, 1904, 10, 450.

[8] Griessmayer, *J. Chem. Soc.*, 1872, 25, 1130; Donath, *Woch. f. Brau.*, 1900, [10], *Allgem. Anzeiger f. Brau*, 16, [24], 561, 562, from *J. Soc. Chem. Ind.*, 1900, 19, 549.

[9] Martin, *Industrial Chemistry, Organic* (Crosby Lockwood & Son), 1920, p. 192.

[10] Schott, *Dingl. poly. J.*, 1871, 202, 52; Birnbaum and Wittich, *Ber.*, 1880, 13, 651.

[11] Welter and Gay-Lussac, *Ann. Chim. Phys.*, 1819, [2], 10, 312; Pape, *Pogg. Annalen*, 1870, 139, 224; Heeren, *ibid.*, 1826, 7, 178.

[12] Topsöe, *Sitzungsber. K. Akad. Wiss. Wien*, 1872, [2], 66, 5.

[13] Bichat, *Compt. rend.*, 1873, 77, 1189; *Bull. Soc. chim.*, 1873, [2], 20, 436.

Calcium Trithionate, CaS₃O₆.—Baumann obtained this compound as a white, crystalline, hygroscopic mass by gently warming calcium dithionate solution with sulphur for two days and then evaporating.[1] Apparently, however, this has not been confirmed.[2]

Calcium Sulphate, CaSO₄, occurs naturally in two forms—*gypsum* and *anhydrite*. The former, crystallising with 2 molecules of water, is more frequently met than the latter, which, as its name indicates, is anhydrous. There are several varieties of gypsum : rock or massive gypsum, density 2·30–2·33, composed of minute crystals : large monoclinic crystals, often twinned, of selenite, which can be split into sheets and is the standard for the second degree of hardness in Mohs' scale ; fibrous gypsum, or *satin-spar* ; a compact, crystalline, slightly translucent form of rock gypsum, used for purposes of ornament and known as *alabaster* ;[3] and, finally, *gypsite*, formed by the evaporation of gypsiferous waters as a soft, incoherent, earthy deposit. Gypsum is often found interstratified with limestone and may have originated in the interaction of the limestone with soluble sulphates, with sulphuric acid resulting from the decomposition of sulphides, or with sulphurous vapours and solutions of volcanic origin. It is found in most countries. Anhydrite occurs as thin seams in rock salt, as large masses coated with gypsum produced by hydration of the anhydrite, or as a replacement of limestone. Local uplifts, and fracture or crumpling of rocks, are often caused by the hydration of subterranean beds of anhydrite.[4]

Calcium sulphate is also a constituent of certain minerals : for example, *glauberite*, $CaNa_2(SO_4)_2$; *syngenite*, $CaK_2(SO_4)_2.H_2O$; *polyhalite*, $Ca_2K_2Mg(SO_4)_4.2H_2O$; *penta-salt*, $Ca_5K_2(SO_4)_6.H_2O$; and *krugite*, $Ca_4K_2Mg(SO_4)_6.2H_2O$. The conditions for the formation of these minerals in oceanic salt deposits have been studied by van 't Hoff and his colleagues.[5]

Calcium sulphate is largely responsible for the permanent hardness in natural waters.

Calcium Sulphate Dihydrate, $CaSO_4.2H_2O$, is formed by the precipitation of soluble salts of calcium by alkali sulphates, or by neutralisation of the carbonate or oxide by dilute sulphuric acid. For technical purposes, however, natural gypsum is almost exclusively employed. In Great Britain alone, between 1903 and 1916, the average annual output was 250,000 tons.[6]

In addition to the forms already mentioned, a hemihydrate, $2CaSO_4.H_2O$, and certain allotropic modifications of anhydrite can be prepared. Although these are of considerable commercial importance and have been the object of much careful study, the literature on the

[1] Baumann, *Jahresber.*, 1845, 202.

[2] Kessler, *Pogg. Annalen*, 1848, 74, 249 ; *Annalen*, 1848, 68, 233.

[3] Alabaster has been prepared artificially by heating hydrated sodium sulphate and anhydrous calcium chloride together for about six hours at 300–310° C. under a pressure of 12·5 atmospheres, see Copisarow, *Trans. Chem. Soc.*, 1923, 123, 796.

[4] On occurrence of gypsum and anhydrite, see Stone and others, " Gypsum Deposits of United States," *U.S. Geol. Surv.*, 1920, Bull 697.

[5] van 't Hoff, *Zeitsch. anorg. Chem.*, 1905, 47, 244 ; *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 935 ; and Voerman, *ibid.*, 984 ; van 't Hoff, Voerman, and Blasdale, *ibid.*, 1905, 305 ; van 't Hoff and d'Ans, *ibid.*, 478 ; van 't Hoff, Farup, and d'Ans, *ibid.*, 1906, 218 ; van 't Hoff and d'Ans, *ibid.*, 412. See also Anderson and Nestell, *J. Ind. Eng. Chem.*, 1920, 12, 243.

[6] *J. Soc. Chem. Ind.*, 1918, 37, 201R.

subject is full of contradictions as to the conditions of their formation and the relations between them.

Calcium sulphate may also be precipitated in a gelatinous form by the action of sulphuric acid on a methyl alcoholic solution of calcium oxide,[1] or by the addition of alcohol to an equal volume of a saturated solution of calcium sulphate.[2]   It contains more water than gypsum, but no combined alcohol.   It is also more soluble than gypsum.

Calcium Sulphate Hemihydrate or Plaster of Paris, $2CaSO_4.H_2O$.— When gypsum is heated between 100° and 200° C., a product is obtained corresponding to the formula $2CaSO_4.H_2O$.[3]   This possesses the property of hydrating again and setting to a hard mass, which expands during solidification, thus giving a sharp impression of the mould in which it is placed.   In reality there is a total contraction, made up of a preliminary contraction, followed by a smaller expansion.   The reaction takes place with considerable heat evolution.   From the fact that deposits of gypsum at Montmartre were first used for the production of this compound on an extensive scale, it received the name of plaster of Paris.

In the manufacture of plaster of Paris the maximum temperature employed in England is 110°-120° C., and in Germany 130° C.   In America 180°–200° C. is often reached, although it may also be discharged at 120° C.   The transition temperature from gypsum to the half-hydrate is 107° C.,[4] but this does not exclude the possibility of carrying out the dehydration at a still lower temperature, provided the vapour pressure is reduced by a current of dry air,[5] or by the use of an open crucible.[6]   In England the gypsum is heated in an oven in which it is piled in lumps upon arches under which the fuel is burnt.   In America the gypsum is often finely ground before being heated in pots or kettles 8–14 feet in diameter and 6–10 feet deep, and made of boiler plates with a convex iron or steel bottom.   The gypsum is stirred.   The agitation of the powder by the escaping water vapour is described as "boiling."   This method produces a good quality of plaster, but it is slow and expensive and is being gradually replaced by the use of rotary heaters.[7]

The hemihydrate forms rhombic crystals, which, through repeated twinning, appear hexagonal.[8]   The density is 2·63.[9]   On exposure to air, moisture is absorbed with gradual formation of gypsum.   The hemihydrate has been found as a crystalline deposit in boilers working at two atmospheres pressure.[10]

Davis stated that when freshly prepared crystals of gypsum are heated for three or four hours with water at 100° C., a half-hydrate,

[1] Neuberg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 820.

[2] Cavazzi, *Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 196.

[3] Le Chatelier, *Recherches expt. sur la Const. des Mort. hydraul.*, 1904; *Compt. rend.*, 1883, 96, 1668.

[4] van 't Hoff and others, *Zeitsch. physikal. Chem.*, 1903, 45, 257.

[5] Guareschi, *Atti Acc. Torino*, 1915, 50, 881; Gaudefroy, *Compt. rend.*, 1914, 158, 2006.

[6] Davis, *J. Soc. Chem. Ind.*, 1907, 26, 732.

[7] Thorpe, *Dictionary of Applied Chemistry* (Longmans, Green & Co.), 1921, vol. i., p. 749, Desch, *The Chemistry and Testing of Cement*, 1911 (Arnold); Stone, *loc. cit.*; Dancaster, *Limes and Cements* (Crosby Lockwood & Son), 1916, ch. viii.

[8] Grengg, *Zeitsch. anorg. Chem.*, 1914, 90, 327.

[9] Gaudefroy, *loc. cit.*

[10] Johnston, *Phil. Mag.*, 1838, [3], 13, 325.

which sets very slowly, is obtained.[1] This appears to be identical with a half-hydrate obtained by Le Chatelier in a similar way at 130°–150° C.,[2] and Davis thought that it might be a second modification. Probably it is merely in a less finely divided state than ordinary plaster.

The Setting of Plaster of Paris.—Calcium sulphate is only very slightly soluble in water, but it has a great tendency to form supersaturated solutions.[3] Le Chatelier attributed to this phenomenon the setting of plaster.[4] He supposed that the partially dehydrated calcium sulphate dissolves, forming a solution which is supersaturated with respect to gypsum. From this solution is deposited hydrated sulphate as interlocking needles which offer great frictional resistance to disruption. The breaking of set plaster is not due to fracture of the crystals themselves, as in the case of metals, but to the overcoming of the forces of cohesion at the crystal surfaces.[5] According to Davis,[1] the plaster on setting first forms orthorhombic crystals which slowly change to monoclinic, the two changes corresponding with the observed contraction and expansion respectively. Recent views, however, require the existence of an intermediate colloidal state from which crystallisation takes place.[6]

The rate of setting depends on the time and temperature of calcination of the gypsum.[7] It is also greatly influenced by the presence of small quantities of foreign substances, some of which retard whilst others accelerate it.[8] Rohland and others showed that those substances which increase the solubility of calcium sulphate also increase the rate of setting of plaster of Paris, and *vice versa.* Sulphates, chlorides, nitrates, bromides, and iodides of potassium, sodium, and ammonium, potassium hydroxides, sulphuric, hydrochloric, and nitric acids, sulphates of zinc, iron, and copper, calcium oxide, soap, potassium dichromate, ammonium fluoride, aluminium sulphate and chloride, lithium chloride and magnesium chloride accelerate the rate of setting. Boric acid, borax, sodium and potassium silicates, sodium, calcium, and magnesium carbonates, glycerol, and alcohol retard it.

Haddon,[9] on rather insufficient grounds, appears to consider that Rohland's theory is not entirely justifiable.

Emulsoids, such as gum acacia, glue, etc., retard the setting in consequence of adsorption,[10] and this fact is made use of by artists and modellers.

[1] Davis, *loc. cit.*

[2] Le Chatelier, *Ann. Mines*, 1887, [8], 11, 345.

[3] Marignac, *Ann. Chim. Phys.*, 1874, [5], 1, 274.

[4] Le Chatelier, *loc. cit.*, and *Compt. rend.*, 1883, 96, 715, 1056; see also Chaey, *Bull. Soc. chim.*, 1903, [3], 29, 171.

[5] Haddon, *J. Soc. Chem. Ind.*, 1921, 40, 122T.

[6] Rohland, *Zeitsch. anorg. Chem.*, 1904, 40, 182; 1914, 89, 352; *Kolloid.-Zeitsch.*, 1913, 13, 61; Ostwald and Wolski, *ibid.*, 1920, 27, 78; Traube, *ibid.*, 1919, 25, 62; Cavazzi, *Gazzetta*, 1912, 42, ii., 626.

[7] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1893, 25, 207.

[8] Schott, *Dingl. poly. J.*, 1870, 196, 357; Ditte, *Ann. Chim. Phys.*, 1898, [7], 14, 204; Rohland, *Ber.*, 1900, 33, 2831; *Zeitsch. anorg. Chem.*, 1902, 31, 437; 1903, 35, 194, 201; 1904, 40, 182; 1914, 89, 352; *Zeitsch. angew. Chem.*, 1905, 18, 327; *Zeitsch. Elektrochem.*, 1908, 14, 421; *Handbuch d. anorg. Chem.*, Abegg (S. Hirzel), Leipzig, 1905, vol. ii., p. 180; see also Astruc and Canals, *J. Pharm. Chim.*, 1916, 13, 214; Canals, *ibid.*, 1916, 14, 33, 78; Traube, *loc. cit.*

[9] Haddon, *J. Soc. Chem. Ind.*, 1920, 39, 165T.

[10] Friend and Vallance, *Trans. Chem. Soc.*, 1922, 121, 166.

Anhydrous Calcium Sulphate.—Natural anhydrite crystallises in the rhombic system and has a density of 2·8–3·0 and hardness 3–3·5. It gradually hydrates to gypsum in the presence of water, but does not set unless ground to an extremely fine powder.[1] The hydration is influenced by foreign substances in the same way as the setting of plaster of Paris.

It may be prepared artificially by fusing calcium chloride with potassium sulphate and dissolving out the potassium chloride with water.[2]

Two modifications of anhydrite are obtained by heating the hemihydrate.[3] The first one, formed under 200° C., takes up water very quickly, probably forming the hemihydrate almost instantaneously and passing more slowly to gypsum.[4] This variety differs from the natural form and is known as soluble anhydrite. It forms triclinic needles[5] of density 2·45.[6] Van 't Hoff and his co-workers obtained it by dehydrating precipitated calcium sulphate *in vacuo* at 60°–90° C. over phosphorus pentoxide or sulphuric acid, or by shaking plaster of Paris with twenty times its weight of water at 100° C.[7]

By heating soluble anhydrite to bright redness another compound is formed which hydrates very slowly and does not harden, and is probably identical with natural anhydrite.[5] Hoppe-Seyler[8] apparently obtained it by heating gypsum with a concentrated solution of sodium chloride in a sealed tube at 125°–130° C. A temperature a little above 30° C. is sufficient however.[7]

At high temperatures an anhydrous form, capable of both hydration and setting, is obtained.[9] It sets more slowly than plaster of Paris, but forms a very hard and highly resistant plaster which finds technical application under the name of *Estrich gypsum* or *flooring plaster*. The rate of setting can also be accelerated or retarded by suitable catalysts, but the same substances do not necessarily produce the same effect as in plaster of Paris.

At high temperatures dead-burnt gypsum, which will neither hydrate nor set, is also produced, and there are two rival theories as to the nature of Estrich gypsum and dead-burnt gypsum. According to van 't Hoff, the rate of setting continuously falls as the temperature of burning is increased. If the temperature is raised so high that the setting and hydrating power disappear, the crystalline structure is lost and the plaster is then dead burnt. From the work on soluble and insoluble anhydrite, Estrich gypsum would thus appear to be a mixture of the two. The proportions, and, therefore, the setting power, depend on the temperature of calcination—dead-burnt gypsum being obtained when the temperature is high enough to transform all the soluble into insoluble anhydrite.

[1] Hartner, *Zeitsch. angew. Chem.*, 1920, 33, i., 175.

[2] Manross, *Annalen*, 1852, 82, 353.

[3] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1894, 26, 170, 221 ; 1895, 27, 256 ; *Zeitsch. anorg. Chem.*, 1894, 7, 432, 433 : Lacroix, *Compt. rend.*, 1898, 126, 360, 553 ; Cloez, *Bull. Soc. chim.*, 1903, [3], 29, 169, 171.

[4] Cloëz, *loc. cit.*

[5] Lacroix, *loc. cit.*

[6] Gaudefroy, *loc. cit.*

[7] van 't Hoff, *Zeitsch. physikal. Chem.*, 1903, 45, 257.

[8] Hoppe-Seyler, *Pogg. Annalen*, 1866, 127, 161.

[9] Rohland, *Zeitsch. anorg. Chem.*, 1903, 35, 194.

Rohland, on the other hand, considered that Estrich gypsum is formed at a higher temperature than dead-burnt gypsum.[1] Hence arose the belief, denied, however, by van 't Hoff,[2] that the former might be a basic sulphate. Von Glasenapp favoured the latter view, and stated that Estrich gypsum may be produced at a temperature, namely 900°–1000° C., or even 1300° C., much higher than is usually considered suitable, and a considerable amount of calcium oxide may be present before the product is incapable of hardening.[3] He observed glassy and crystalline portions ; the first he regarded as a solid solution of lime in neutral sulphate, and the second as pure anhydrite.

Grengg studied the dehydration products of gypsum under the microscope, and also concluded that the formation of dead-burnt gypsum takes place first.[4] He regarded it as completely dehydrated calcium sulphate, probably identical with natural anhydrite. He also regarded calcium oxide as one of the constituents of Estrich gypsum, and, like von Glasenapp, found a combination of a glassy and crystalline structure, but supposed both to be solid solutions of calcium oxide in the sulphate—the proportions and concentrations of these varying with the time and temperature of heating.[5] Observations on the temperature of formation of the oxide seem to cast doubt on the basic sulphate theory.[6] When calcium sulphate is heated to constant weight at 1000° C. only 0·21 per cent. of oxide is formed, at 1300° C. 3·0 per cent., and at 1375° C. 98·67 per cent., the salt then melting. The rate becomes much more rapid above 1380° C.[6]

It is possible that the supposed modifications of anhydrite owe their differences largely to differences merely in the fineness of their particles.[7]

When calcium sulphate is strongly heated there is a transition point at 1193° C.[8] The α-form stable above the transition point is completely miscible with α-strontium sulphate, and is, therefore, isomorphous with it and with α-barium sulphate.

The melting-point of calcium sulphate is 1450° C.[8] According to Calcagni and Mancini, pure calcium sulphate decomposes so rapidly at 1000° C. that the melting-point cannot be determined directly, but extrapolation from the freezing-point curve of sodium and calcium sulphates gave 1375° C.[9]

Gallo suggested a scheme for the estimation of the different modifications of calcium sulphate in plaster of Paris which depends on the amount of water given up or absorbed under different conditions.[10]

The Vapour Pressure and Solubility Relations between the different Modifications of Calcium Sulphate.—The equilibrium relations between gypsum, the half-hydrate, soluble anhydrite, and natural anhydrite, between

[1] Rohland, *Zeitsch. anorg. Chem.*, 1909, **65**, 105.

[2] van 't Hoff, *loc. cit.*

[3] von Glasenapp, *Tonind. Zeit.*, 1908, **32**, 1148, 1197, 1230.

[4] Grengg, *Zeitsch. anorg. Chem.*, 1914, **90**, 327 ; see also Gallo, *Gazzetta*, 1914, **44**, i., 497.

[5] See also Hartner, *Zeitsch. angew. Chem.*, 1920, **33**, i., 175, who obtained a cement by adding lime to anhydrite.

[6] Budnikov and Syrkin, *Chem. Zeit.*, 1923, **47**, 22 ; see also Cobb, *J. Soc. Chem. Ind.*, 1910, **29**, 69.

[7] Desch, *Trans. Ceramic Soc.*, 1918–19, **18**, 15.

[8] Grahmann, *Zeitsch. anorg. Chem.*, 1913, **81**, 257.

[9] Calcagni and Mancini, *Atti R. Accad. Lincei*, 1910, [5], **19**, ii., 422 ; but contrast Budnikov and Syrkin, *loc. cit.*

[10] Gallo, *Gazzetta*, 1914, **44**, i., 497.

0° and 100° C., have been studied by van 't Hoff and his co-workers.[1] According to the phase rule, the system calcium sulphate and water has one degree of freedom when three phases are present for example, solid, solution, and vapour, or two solids and vapour; but reaches an invariant point when four phases appear for example, two solids, solution, and vapour. Van 't Hoff followed the change of vapour pressure with composition and obtained the results recorded in the following table :—

Temp., °C.	Vapour Pressure of Water or Saturated Solution of Dihydrate (I.)	Gypsum in contact with		
		Half-hydrate (II.)	Sol Anhyd. (III.).	Nat Anhyd. (IV.).
	mm.	mm.	mm	mm.
0	4 57	1·17	1 52	2·06
5	6 51	1 84	2 34	3·17
10	9 14	2 78	3 55	4·79
15	12·7	4 21	5 29	7 12
20	17·4	6·24	7 77	10 5
30	31·5	12 7	16 1	21·6
40	54 9	26 3	31·8	42 5
50	92 0	50 0	59 9	79·7
60	149	91·4	108	143
65	187	122	143	175 (*at* 63·5° C.)
75	289	210	245	
90	526	446	513	
95	634	565	588 (*at* 93° C.)	
105	906	888		
110	1073	971 (*at* 107° C.)		

Consider first columns I. and IV. As saturated solutions of calcium sulphate are very dilute, the vapour pressure curve of a saturated solution of gypsum is practically the same as for water. At 63·5° C. natural anhydrite and a saturated solution of gypsum have the same vapour pressure, 175 mm., and are therefore in equilibrium with one another. The vapour pressure curves of gypsum and natural anhydrite meet at that point. Below 63·5° C. the vapour pressure of the anhydrite is the lower, which means that the anhydrite is unstable with respect to the dihydrate and, if treated with water below this temperature, should be transformed into the dihydrate. On the other hand, at higher temperatures than this, the anhydrite is the stable form and should be ultimately produced from the dihydrate, although the change is not necessarily a rapid one. Similarly, the transition point of gypsum into soluble anhydrite is 93° C., and of gypsum into plaster of Paris or hemihydrate 107° C. The hemihydrate, however, will still be unstable with respect to soluble anhydrite and natural anhydrite, and soluble anhydrite with respect to natural anhydrite.

[1] van 't Hoff and others, *Zeitsch. physikal. Chem.*, 1903, **45, 257.**

In the presence of concentrated solutions of other salts, such as sodium or magnesium chlorides, these transition points are lowered. For example, a saturated sodium chloride solution lowers the temperature of equilibrium between gypsum and natural anhydrite to 36° C.

This explains the production of natural anhydrite from gypsum by heating with concentrated sodium chloride solution a little above 30° C. It also explains the existence of anhydrite in contact with beds of rock salt. The inter-relations of gypsum, natural anhydrite, soluble anhydrite, and the half-hydrate, account for the fact that only the two former are found in nature, since the two latter are always unstable with respect to both the others.

The energies of transformation of the different modifications into gypsum are given by van 't Hoff as follows :—

> From half-hydrate   737 − 6·88t small cal. (t in ° C.).
>
> „   soluble anhydrite 602 − 6·48t „   „
>
> „   natural   „   435 − 6·84t „   „

The solubilities of gypsum and soluble and natural anhydrite were studied by Melcher by means of electrical conductivity determinations. His results are combined with some of other investigators in the following table [1] :—

Form.	Solubility in Milli-equivalents per Litre at Temperatures, ° C.										
	0	18	30	40	50	65	75	100	156	200	218
Gypsum .	25·9	29 5	30·7	30·8	30·0	28·3	27·1	23 3	.	.	..
Sol. Anhyd. .	..	..	..	..	..	.	..	22·8	6·4	2·3	..
Nat. Anhyd. .	..	..	..	..	..	.	..	9·2	2 7	0·9	0·7

The solubility curves for the three compounds are given in Fig. 2. The transition points as found by van 't Hoff are represented by the points where the solubility curves for the two anhydrites meet that for gypsum. Soluble anhydrite is evidently a meta-stable form. No determinations, other than qualitative ones,[2] have been made for plaster of Paris, but presumably the solubility curve for this substance would show higher values than soluble anhydrite at the same temperature, and would cut the curve for gypsum at about 107° C. Jänecke [3] confirmed van 't Hoff's observation that gypsum melts at 107° C., giving the hemihydrate.

The solubility curve for gypsum shows a maximum at about 40° C., the solubility being 30·826 milli-equivalents per litre. Earlier investigators found a slightly lower temperature, 38° C.[4]

An observation of Hulett's [5] explains the difficulty found in arriving

[1] Melcher, J. Amer. Chem. Soc., 1910, 32, 50 ; Hulett and Allen, ibid., 1902, 24, 667 ; Boyer-Guillon, Ann. Conserv. Arts Mét., 1900, [3], 2, 187 ; Tilden and Shenstone, Phil. Trans., 1884, 175A, 23 ; Kohlrausch, Zeitsch. physikal. Chem., 1908, 64, 129.
[2] Droeze, Ber., 1877, 10, 330.
[3] Jänecke, Zeitsch. physikal. Chem., 1915, 90, 265.
[4] Marignac, Ann. Chim. Phys., 1874, [5], 1, 274 ; Droeze, loc. cit.
[5] Hulett, J. Amer. Chem. Soc , 1905, 27, 49 ; see also W. J. Jones and Partington, Phil. Mag., 1915, [6], 29, 35 ; M. Jones and Partington, Trans. Chem. Soc., 1915, 107, 1019 ; Namba, J. Soc. Chem Ind., 1921, 40, 279T.

at concordant solubility values. By shaking powdered gypsum with water he obtained a supersaturated solution which required seventeen
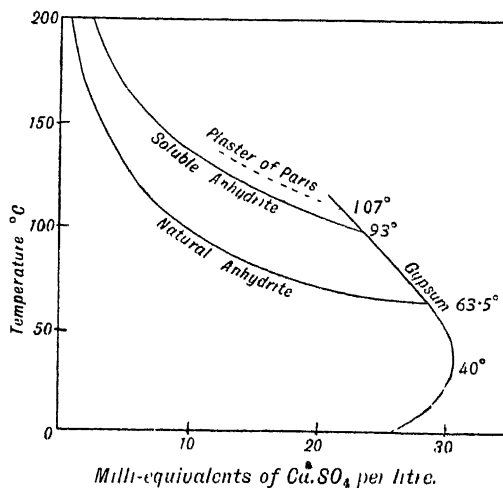
Fig. 2.—Solubility of calcium sulphate.

days to reach a state of final equilibrium. The degree of supersaturation depends on the size of the particles.

There is apparently a considerable difference between the rates of solubility at the different surfaces of a selenite crystal, although the actual solubilities are naturally the same in each case.[1]

Gypsum is almost insoluble in alcohol but slightly soluble in glycerol,[2] 0·0072 gram-molecule per litre, the solubility increasing with temperature.

The solubility in water is greatly increased by the presence of acids. The following values have been obtained[3] :—

Ce containing 1 mgm.-equivalent of Acid.	Increase in Solubility at 20° C. in mgm. per mgm.-equivalent of Acid.			
	HCl.	HNO₃.	CH₂ClCOOH.	CH₃COOH.
0·5	7·61	9·27	..	..
1	11·51	13·1	0·41	0·31
2	15·75	20·4	0·17	..
10	23·0	23·4	..	..

The solubility in different salt solutions has been studied by a number of investigators.[4]

[1] Tolloczki, *Bull. Acad. Sci. Cracow*, 1910, 209, see *J. Chem. Soc*, 1911, **100** Abs. ii., 24.
[2] Asselin, *Compt. rend.*, 1873, **76**, 884
[3] Ostwald and Banthisch, *J. prakt. Chem.*, 1884, [2], **29**, 52.
[4] Droeze, *Ber.*, 1877, **10**, 330 ; Tilden and Shenstone, *Proc. Roy. Soc.*, 1885, **38**, 331 ; Lunge, *J. Soc. Chem. Ind.*, 1885, **4**, 31 ; Cohn, *J. prakt. Chem.*, 1887, [2], **35**, 43 ; Ditte,

Calcium sulphate gives a brilliant green cathode-ray fluorescence if a trace of manganese be present, and bismuth makes it orange-red.[1]

Double Salts.—Calcium sulphate forms a number of double salts. Some of them resemble, and are isomorphous with, the naturally occurring double salts already mentioned.

Salts.	Remarks.	Authority.
$Ca_2Cu(NH_4)_2(SO_4)_4.2H_2O$	Compare polyhalites,	d'Ans, *Ber.*, 1908, **41**, 1777.
$Ca_2CdK_2(SO_4)_4.2H_2O$	$Ca_2MgK_2(SO_4)_4.2H_2O.$	
$Ca(NH_4)_2(SO_4)_2.2H_2O$	..	Bell and Taber, *J. Physical Chem*, 1907, **11**, 492.
$Ca(NH_4)_2(SO_4)_2.H_2O$	Compare syngenite,	Ditte, *Compt. rend.*, 1877, **84**,
$CaRb_2(SO_4)_2.H_2O$	$CaK_2(SO_4)_2.H_2O.$	86, d'Ans, *Ber.*, 1906, **39**, 3326; 1908, **41**, 1776, Barre, *Compt. rend.*, 1909, **148**, 1601, d'Ans and Zeh, *Ber.*, 1907, **40**, 4912
$Ca_5(NH_4)_2(SO_4)_6.H_2O$	Compare penta-salt, $Ca_5K_2(SO_4)_6.H_2O.$	d'Ans, *Ber.*, 1907, **40**, 192, Barre, *Ann. Chim. Phys.*, 1911, [8], **24**, 145.
$Ca_3(NH_4)_2(SO_4)_4$	..	Barre, *loc. cit*; d'Ans, *Ber.*, 1907, *loc. cit.*
$Ca_3Cs_2(SO_4)_3$	.	d'Ans, *Ber.*, 1908, **41**, 1776.
$Ca_3Rb_2(SO_4)_4$	.	d'Ans and Zeh, *Ber.*, 1907, **40**, 4912.
$Ca_2K_2(SO_4)_3$	..	Grahmann, *Zeitsch. anorg. Chem.*, 1913, **81**, 257.
$Ca_2K_2(SO_4)_3.3H_2O$	..	Ditte, *Compt. rend*, 1877, **84**, 86
$Ca_2Rb_2(SO_4)_3.3H_2O$		
$CaNa_4(SO_4)_3.H_2O$		
$2CaK_2(SO_4)_3.3H_2O$		
$CaNa_2(SO_4)_3.K_2CrO_4.H_2O.$		Hannay, *J. Chem. Soc*, 1877, **32**, 399.
$CaSO_4.2K_2CrO_4,$		
$CaSO_4.K_2CrO_4.H_2O.$		
$CaK_2(SO_4)_2.4H_2O$	..	Ditte, *Ann. Chim. Phys.*, 1898, [7], **14**, 294.
$CaTi(SO_4)_3$	Decomposed by water	Weinland and Kuhl, *Zeitsch. anorg. Chem.*, 1907, **54**, 253.
$CaSn(SO_4)_3.3H_2O$	Derivative of orthostannic acid of type $Sn[(SO_4H)_3(OH)_3]M$	Weinland and Kuhl, *Ber.*, 1906, **39**, 2951.
$CaO.As_2O_3\,3SO_3$	.	Kuhl, *Arch. Pharm.*, 1907, **245**, 377.
$CaSb_2(SO_4)_4.6H_2O$	.	Kuhl, *Zeitsch. anorg. Chem.*, 1907, **54**, 256.

Uses of Calcium Sulphate.—In the form of either plaster of Paris or Estrich gypsum, calcium sulphate forms the principal ingredient of many

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Compt. rend., 1898, **126**, 694; Cameron, *J. Physical Chem.*, 1901, **5**, 556; Cameron and Seidell, *ibid.*, 1901, **5**, 643; Cloez, *Bull. Soc. chim.*, 1903, [3], **29**, 167; d'Anselme, *ibid.*, 1903, [3], **29**, 372; Cameron and Breazeale, *J. Physical Chem.*, 1903, **7**, 571; 1904, **8**, 335; Seidell and Smith, *ibid.*, 1904, **8**, 493; Cameron and Brown, *ibid.*, 1905, **9**, 210; Sullivan, *J. Amer. Chem. Soc.*, 1905, **27**, 529; Cameron and Bell, *J. Physical Chem.*, 1906, **10**, 210; *J. Amer. Chem. Soc.*, 1906, **28**, 1220; Taber, *J. Physical Chem.*, 1906, **10**, 626; Arth and Chrétien, *Bull. Soc. chim.*, 1906, [3], **35**, 778; Taber and Bell, *J. Physical Chem.*, 1906, **10**, 119; 1907, **11**, 637; d'Ans and Schreiner, *Zeitsch. anorg. Chem.*, 1909, **62**, 128; 1910, **67**, 437; Maruelli, *Ann. Chim. Applicata*, 1916, **5**, 13.

[1] de Boisbaudran, *Compt. rend.*, 1886, **103**, 468.

of the cements and wall-plasters on the market—for example, Keene's, Martin's, and Parian cement. A retarder, such as glue or blood, or an accelerator, alum, sodium sulphate, etc., is mixed with it.[1] Stucco is a hard plaster which can be polished, and is obtained by treating plaster of Paris with a lukewarm solution of size, fish-glue, or gum-arabic, or by mixing with freshly slaked lime and dipping the casting in a strong solution of magnesium sulphate, sodium silicate, or alum. Fibrous plaster for temporary buildings is made from plaster toughened by tow, asbestos, or slag wool, and backed by coarse canvas. Gypsum boards and tiles are also made. The tensile strength of plaster is affected by the conditions of gauging, or wetting,[2] and by the added constituents.[3] Gypsum is often put in Portland cement in small quantity to act as a retarder. It is sometimes used in the natural form as building-stone.

There seems to be some doubt as to whether or not calcium sulphate is of any value as a fertiliser. It is probably more advantageous to employ it along with basic rather than with acid fertilisers.[4] It has been suggested that it increases the availability of potash in the soil,[5] but this has not, apparently, been confirmed.[6]

Various patents were taken out in Germany during the war for the manufacture of sulphuric acid from calcium sulphate.[7] The methods proposed consist chiefly in the reduction by coal or hydrocarbons, and the removal and oxidation of sulphuretted hydrogen,[8] or in the decomposition of the sulphate by silicates.

The production of ammonium sulphate from gypsum for use as a fertiliser, has also been suggested.[9]

Calcium sulphate is an ingredient of certain painters' colours, and is employed in paper manufacture for weighting the paper. Plaster of Paris is used in the making of moulds for many purposes, for example, for rubber stamps, pottery, terra cotta, and special foundry castings, also for making statuary, relief maps and models, surgical casts, relief decorations on walls and ceilings, for bedding plate-glass for polishing, and for many other purposes.

Acid Calcium Sulphates.—By cooling, or by precipitation with hot water of saturated solutions of calcium sulphate in hot concentrated sulphuric acid, several different acid sulphates may be obtained, $CaSO_4.H_2SO_4,$[10] $CaSO_4.3H_2SO_4,$[11] and $2CaSO_4.H_2SO_4.$[12] Kendall and Davidson,[13] on studying the solubility curve of calcium sulphate in anhydrous sulphuric acid, found two modifications of the compound

[1] Martin, *Industrial Chemistry, Inorganic* (Crosby Lockwood & Son), 1917, vol. ii., p. 113; Thorpe, *Dictionary of Applied Chemistry* (Longmans, Green & Co.), 1921, vol. i., p. 748.

[2] Haddon, *J. Soc. Chem. Ind.*, 1921, 40, 122T

[3] Troxell, *Amer. J. Sci.*, 1916, [4], 41, 198.

[4] Nolti, *J. Landwirt.*, 1917, 65, 67. see *J. Chem. Soc.*, 1917, 112, Abs. i., 624; see also Takeuchi, *Bull. Coll. Agr. Tokyo*, 1908, 7, 583, see *J. Chem. Soc.*, 1908, 94, Abs. ii., 624.

[5] Briggs and Breazeale, *J. Agric. Res.*, 1917, 8, 21, see *J. Soc. Chem. Ind.*, 1917, 36, 328; McMiller, *J. Agric. Res.*, 1918, 14, 61, see *J. Soc. Chem. Ind.*, 1918, 37, 555A.

[6] Russell, *App. Chem. Reports*, 1918, 3, 353.

[7] Ewan, *ibid.*, 1920, 5, 174.

[8] Riesenfeld, *J. prakt. Chem.*, 1920, [2], 100, 115.

[9] Wride, *Chem. Age*, 1920, 2, 32

[10] Berzelius, *Annalen*, 1843, 46, 241.

[11] Schultz, *Pogg. Annalen*, 1868, 133, 137.

[12] Willoughby, *Trans. Roy. Soc. Canada*, 1913, 7, 211; see also Garside, *Chem. News*, 1875, 31, 245.

[13] Kendall and Davidson, *J. Amer. Chem. Soc.*, 1921, 43, 979.

$CaSO_4.3H_2SO_4$.   Only one of them was stable over the range of temperature of the experiment, namely 0°–63° C. These compounds are all decomposed by water or by moist air.   The compound $CaSO_4.H_2SO_4$ has been obtained in the gelatinous state.[1]   D'Ans separated an acid double sulphate of calcium and sodium, but it was probably an isomorphous mixture.[2]

Calcium Pyrosulphate, CaS_2O_7, is obtained by heating together calcium sulphate and sulphur trioxide in a sealed tube. It readily attracts moisture from the air and great heat is developed on bringing it into contact with water.[3]

CALCIUM AND SELENIUM.

Calcium Selenide, CaSe.—Selenium will unite directly with calcium at red heat to form the selenide.[1]   The heat of formation is 77·06 Cal.[5]   It can be prepared by the reduction of calcium selenate at 400° C. by hydrogen,[6, 7] by heating selenium with lime when a black mixture of selenide and selenite is obtained, or by precipitation of a soluble calcium salt by potassium selenide.[8]

Calcium selenide is a white substance which becomes red on exposure to air owing to the liberation of selenium by the action of carbon dioxide.[6, 7]   It is soluble in dilute acids and is decomposed by water.[7] It can be obtained in the phosphorescent state by admixture with a suitable phosphorogen, copper, bismuth, manganese, nickel, antimony, etc.[9]   The intensity and duration of the phosphorescence is much smaller than in the case of the sulphides.   The position of brightest phosphorescence in the spectrum is at a longer wave-length than in either the sulphur or oxygen compounds,[10] and the upper wave-length above which the selenides are inactive is, in general, lower than for the corresponding sulphides.

Calcium Selenite, $CaSeO_3$, can be obtained in the anhydrous form as crystalline grains by the action of selenious acid on calcium carbonate.[11] It is not very soluble in water.   The hydrate, $3CaSeO_3.4H_2O$, is obtained in prismatic crystals by the action of sodium selenite on calcium chloride solution, and a dihydrate, $CaSeO_3.2H_2O$, in silky efflorescent crystals, can also be prepared.[12]

An anhydrous acid salt, $CaSeO_3.SeO_3$, is deposited at 60° C. from acid solutions of the selenite, and by evaporation at ordinary temperatures, the compound $CaH_2Se_2O_6.H_2O$ can be obtained in prisms and in hexagonal plates which are very soluble in water and unchanged by exposure to the atmosphere.[13]

[1] Rohland, *Zeitsch. anorg. Chem.*, 1910, 66, 206.
[2] d'Ans, *ibid*, 1907, 53, 419.
[3] Schulze, *Ber.*, 1884, 17, 2705.
[4] Moissan, *Ann. Chim. Phys.*, 1899, [7], 18, 289.
[5] de Forcrand, *ibid.*, 1911, [8], 24, 256 ; Fabre obtained 58·9 Cal., *ibid.*, 1887, [6], 10, 472.
[6] Fabre, *loc. cit.* ; *Compt. rend.*, 1886, 102, 1469.
[7] Henglein and Roth, *Zeitsch. anorg. Chem.*, 1923, 126, 227.
[8] Berzelius, *Ann. Chim. Phys.*, 1818, [2], 9, 225.
[9] Pauli, *Ann. Physik*, 1912, [4], 38, 870 ; Kittlemann, *ibid.*, 1915, [4], 46, 177.
[10] Schmidt, *ibid.*, 1920, [4], 63, 264.
[11] Muspratt, *J. Chem. Soc.*, 1850, 2, 105.
[12] Nilson, *Bull. Soc. chim.*, 1874, [2], 21, 253 ; 1875, [2], 23, 353.
[13] Nilson, *loc. cit*   See also Muspratt, *loc. cit.*

Calcium Selenate, CaSeO$_4$, can be obtained as transparent or milk-white rhombic prisms, showing double refraction, by fusion of an alkali selenate with sodium and calcium chlorides.[1] It can only be fused with difficulty in the blow-pipe, and it is slowly attacked by hydrochloric acid with evolution of chlorine. The density is 2·93 and the hardness 3·5.

The dihydrate, CaSeO$_4$.2H$_2$O, in monoclinic crystals isomorphous with gypsum, is obtained by mixing solutions of potassium selenate and calcium nitrate and boiling, when the crystals, being less soluble in hot water than in cold, are deposited. When dehydrated by heat and treated with water, it sets like plaster.[2] The density is 2·676.

CALCIUM AND TELLURIUM.

Calcium Telluride.—Calcium unites directly with tellurium at red heat.[3] An impure sample may also be obtained by reducing calcium tellurate with hydrogen at 410° C.[4]

Calcium Tellurite, CaTeO$_3$, is obtained as a flocculent precipitate soluble in boiling water, by the action of tellurious acid on a soluble calcium salt. It is not readily fusible. Berzelius also mentions two acid salts, CaO.2TeO$_2$, or CaH$_2$Te$_2$O$_6$, and CaO.4TeO$_2$, or CaH$_2$Te$_4$O$_{10}$.[5] They melt at white heat, and on cooling form an opaque mass consisting of mica-like scales.

Calcium Tellurate, CaTeO$_4$, is formed as a white flocculent precipitate by the action of sodium tellurate on calcium chloride. The hot aqueous solution gives a powdery deposit on evaporation.[5]

CALCIUM AND CHROMIUM.

Calcium Chromite, CaCr$_2$O$_4$ or CaO.Cr$_2$O$_3$, may be obtained as an olive-green crystalline powder by heating together potassium dichromate and calcium chloride, and extracting with concentrated hydrochloric acid.[6] On precipitating a solution of chrome alum and a calcium salt with potassium hydroxide in excess, a green insoluble compound, corresponding in composition with the formula 2CaO.Cr$_2$O$_3$.xH$_2$O, is formed.[7] It is less stable than the former compound, being readily oxidised to chromate by heating in air. By heating chromium sesquioxide and calcium oxide together in the electric furnace, hard green crystalline plates of density 4·8 and composition 4CaO.Cr$_2$O$_3$ are formed.[8] They are decomposed by water.

Calcium Chromate, CaCrO$_4$, may be obtained by fusing a mixture of calcium chloride with potassium and sodium chromate. It crystallises in fine needles.[9] It may be precipitated from a concentrated solution of a calcium salt with sodium chromate, or formed by the action of chromic acid on calcium carbonate.[9] Reddish-yellow

[1] Michel, *Compt. rend.*, 1888, 106, 878; *Bull. Soc. chim.*, 1888, [2], 49, 29.
[2] von Hauer, *Sitzungsber. K. Akad. Wiss. Wien*, 1860, 39, 299.
[3] Moissan, *loc. cit.*
[4] Henglein and Roth, *Zeitsch. anorg. Chem.*, 1923, 126, 227.
[5] Berzelius, *Ann. Chim. Phys.*, 1835, [2], 58, 225.
[6] Gerber, *Bull. Soc. chim.*, 1877, [2], 27, 433; Dutau, *Compt. rend.*, 1895, 121, 689.
[7] Pelouze, *Ann. Chim. Phys.*, 1851, [3], 33, 5.
[8] Dufau, *ibid.*, 1897, [7], 12, 257; Moissan, *ibid.*, 1895, [7], 4, 136.
[9] Bourgeois, *Compt. rend.*, 1879, 88, 382.

crystals of the dihydrate are usually obtained. Calcium chromate is prepared industrially by the action of the oxygen of the air on a strongly heated mixture of powdered chrome iron and lime.[1] It is used as a pigment.

Calcium chromate is much more soluble in both water and alcohol than the corresponding strontium and barium salts, and this affords a means of separation from the latter.[2]

The relations between anhydrous calcium chromate and its different hydrates have been carefully studied by Mylius and von Wrochem.[3] The α-dihydrate, $CaCrO_4.2H_2O$, forms yellow monoclinic crystals isomorphous with gypsum. These effloresce when exposed to air, and when in contact with a saturated solution pass readily into the rhombic β-dihydrate.[4] At 12° C. the β-compound loses water and passes into a rhombic monohydrate, $CaCrO_4.H_2O$. In contact with a solution at 100° C., especially if mixed with calcium chloride or glycerine, a hemi-hydrate, $2CaCrO_4.H_2O$, also rhombic, is formed. It does not begin to lose its water of crystallisation readily until 400° C. is reached. If a supersaturated solution of calcium chromate is heated above 36° C. the salt gradually separates in the anhydrous form, passing through the intermediate stages of the α-di- and the mono-hydrate. Even after prolonged contact with water the anhydrous form does not pass into the hydrated condition, showing that all the other modifications are unstable with respect to it within the range of temperature considered. This is borne out by the solubility relations, the anhydrous chromate being the least soluble. As may be seen from Fig. 3, the solubility curves of the various forms show no breaks such as would indicate the passage of one modification into another. With the exception of that for the β-dihydrate, the curves all show a decrease of solubility with rise of temperature.

The solubilities at 18° C. are as follows [5] :—

Modification.	α-di-hydrate.	β-di-hydrate.	Mono-hydrate	Hemi-hydrate.	Anhydrous.
Solubility in per cent. $CaCrO_4$	14 3	10·3	9 6	4 4	2 3

Double Salts.—A double potassium calcium chromate in the form of yellow needles, $K_2CrO_4.CaCrO_4.2H_2O$, may be obtained by mixing concentrated solutions of the two salts and shaking for some time.[6] The same salt has been obtained at temperatures below 45° C. in the form of large orthorhombic prisms.[7] In contact with a solution of

[1] Donald, *Ber.*, 1885, 18, 307, ref. Pitt. *ibid.* ; Gilchrist, *ibid.*, 308.

[2] Caron and Raquet, *Bull. Soc. chim.*, 1906, [3], 35, 1061 ; Kolthoff, *Pharm. Weekblad*, 1920, 57, 1080, see *Chem. Zentr.*, 1920, iv., 497.

[3] Mylius and von Wrochem, *Ber.*, 1900, 33, 3689 ; see also Wyrouboff, *Jahresber.*, 1892, 758.

[4] Compare observation by Davis on the formation of an intermediate rhombic form of gypsum in the setting of plaster of Paris, p. 68.

[5] See also Kohlrausch, *Zeitsch. physikal. Chem*, 1908, 64, 158.

[6] Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185.

[7] Barre, *Compt. rend.*, 1914, 158, 495 ; see also Schweitzer, *J. prakt. Chem.*, 1846, [1], 39, 261 ; Rammelsberg, *Pogg. Annalen*, 1855, 94, 516.

potassium chromate at 60° C., these are gradually transformed into small hexagonal prisms of anhydrous salt, $K_2CrO_4.CaCrO_4$.

Rakowski[1] obtained two different modifications of the dihydrate, the α-form belonging to the rhombic system, and the β- to the hemihedral triclinic. The former is unstable with respect to the latter above about
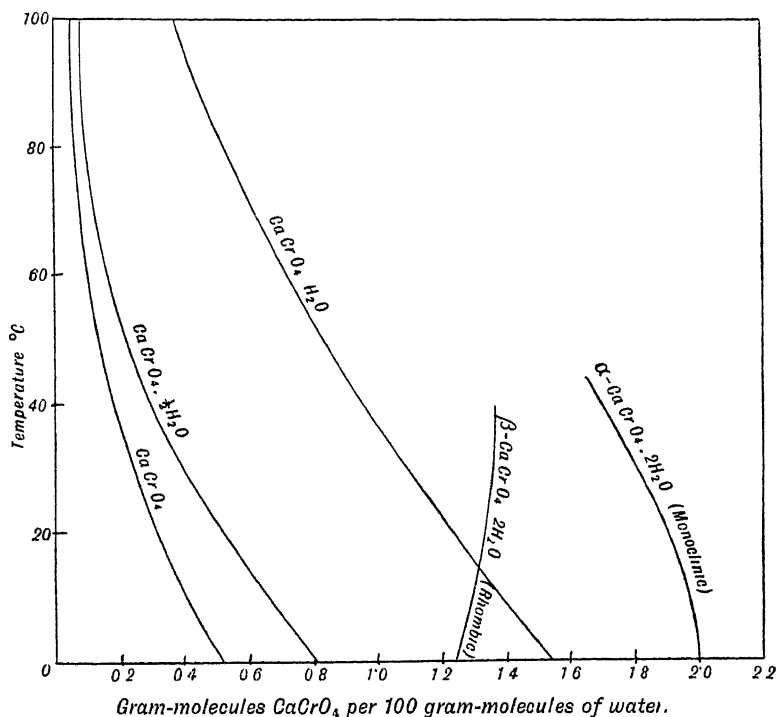
FIG. 3.—Solubility of calcium chromate.

0° C., which is the transition point. The heat of solution of the α-dihydrate is 6·993 Cal., and that of the β-compound 5·459 Cal.

At 97° C. the salt breaks up into its constituents. A solution saturated at 20° C. becomes cloudy at 55°–60° C., and a precipitate is formed at 90°–100° C. corresponding with the formula $K_2CrO_4.4CaCrO_4.25H_2O$.

Several other double salts have been mentioned, $K_2CrO_4.5CaCrO_4$,[2] $K_2CrO_4.4CaCrO_4.2H_2O$,[3] $K_2CrO_4.CaCrO_4.H_2O$, $2K_2CrO_4.CaCrO_4$, and $K_2CrO_4.Na_2CrO_4.CaCrO_4.H_2O$.[4]

Calcium Dichromate, $CaCr_2O_7$, may be obtained by treating a solution of the chromate with sulphuric acid, filtering off the calcium sulphate, and concentrating.[5] Treatment of the neutral chromate with chromic acid, or partial saturation of calcium carbonate with chromic acid, also gives the dichromate as silky yellowish-brown crystals. Both

[1] Rakowski, *Bull. Acad. Sci. St. Petersburg* 1908, **10**, 905, see *J. Chem. Soc.*, 1908, **94**, Abs. ii., 674.
[2] Bahr, *J. prakt. Chem.*, 1853, [1], **60**, 60.
[3] Schweitzer, *loc. cit.*
[4] Hannay, *J. Chem. Soc.*, 1877, **32**, 399.
[5] Donald, *loc. cit.*

a tetrahydrate, $CaCr_2O_7.4H_2O$, as yellowish-red prisms, and a tri-hydrate,[1] $CaCr_2O_7.3H_2O$, forming deliquescent red crystals, are known. It is fairly soluble in water.

Calcium Tetrachromate, $Ca_2Cr_4O_{13}.6H_2O$, is obtained as dark red easily soluble crystals by evaporating over sulphuric acid a solution of chromate containing a large excess of chromic acid.[2]

Basic Calcium Chromate, $Ca_2CrO_5.3H_2O$. Mylius and von Wrochem prepared this compound by saturating chromic acid with milk of lime. It dissolves without decomposition and may possibly be regarded as a derivative of tetrahydric chromic acid.

Calcium Chlorochromate, $Ca(CrO_3Cl)_2.5H_2O$, is a yellow, hygroscopic, crystalline compound melting at $56°$ C.,[3] formed by the action of chromyl chloride on a mixture of chromic acid and calcium carbonate with or without calcium acetate.

CALCIUM AND MOLYBDENUM.

Calcium Molybdate, $CaMoO_4$. Mixed with calcium tungstate, calcium molybdate occurs naturally as a greenish-yellow mineral, *powellite*, of density 5·35. Synthetic powellite has been prepared.[4] By mixing solutions of neutral sodium molybdate and calcium chloride and boiling, or adding alcohol, a white precipitate is obtained.[5] The composition of the strongly calcined product corresponds with that of the neutral salt.[6] By fusing sodium molybdate with sodium and calcium chlorides, and then cooling, a mass of small tetragonal crystals of the salt is obtained.[7]

Calcium molybdate is soluble in acetic acid. The introduction of molybdenum into steel can be satisfactorily effected by the use of calcium molybdate.[8]

Tri-, tetra-, and octo-molybdates are known,[9] and a double ammonium calcium paramolybdate.[10]

Various complex compounds of calcium and molybdenum with iodine,[11] and sulphur,[12] have also been described.

CALCIUM AND TUNGSTEN.

Calcium Tungstate, $CaWO_4$, occurs naturally as the mineral *scheelite*, in which some of the calcium is replaced by molybdenum. It may be obtained by fusing sodium tungstate with calcium chloride,[13] or with a mixture of calcium and sodium chlorides.[14] By the addition of

[1] Bahr, *loc. cit.*
[2] Mylius and von Wrochem, *loc. cit.*
[3] Pràtorius, *Annalen*, 1880, 201, 1.
[4] Michel, *Bull. Soc. min. de France*, 1894, 17, 612.
[5] Ullik, *Annalen*, 1867, 144, 204; Smith and Bradbury, *Ber.*, 1891, 24, 2930.
[6] Smith and Bradbury, *loc. cit.*
[7] Schultze, *Annalen*, 1863, 126, 49; Hiortdahl, *Zeitsch. Kryst. Min.*, 1887, 12, 411.
[8] Kissock, *Chem. Met. Eng.*, 1920, 22, 1018.
[9] Ullik, *loc. cit.* and p. 320; Rosenheim, *Zeitsch. anorg. Chem.*, 1916, 96, 139; Felix, *ibid.*, 1913, 79, 292; Wempe, *ibid.*, 1912, 78, 298.
[10] Rosenheim, *loc. cit.*
[11] Chrétien, *Ann. Chim. Phys.*, 1898, [7], 15, 358; Blomstrand, *Zeitsch. anorg. Chem.*, 1892, 1, 10.
[12] Berzelius, *Pogg. Annalen*, 1826, 7, 261.
[13] Manross, *Annalen*, 1852, 81, 243; 82, 348.
[14] Michel, *Bull. Soc. franç. Min.*, 1879, 2, 142.

a 20 per cent. solution of sodium tungstate to a boiling ammoniacal solution of calcium chloride, the calcium is quantitatively precipitated in a heavy crystalline form as calcium tungstate.[1] It crystallises in octahedra of density about 6.[2] The solubility is approximately 1 part in 500 of water at 15° C.[3]

Crystallised calcium tungstate fluoresces under the influence of X-rays, and may be used for intensifying the photographic effect in X-ray photography.[4]

The specific heat of scheelite is 0·0967.[5]

Several acid calcium tungstates are known : $CaO.2WO_3$ and $CaO.2WO_3.3H_2O$,[3] $3CaO.7WO_3.18H_2O$,[6] $CaO.3WO_3.6H_2O$,[7] and $CaO.4WO_3.10H_2O$.[8]

There are also complex phosphotungstates [9] and silicotungstates,[10] an arsenotungstate,[11] and a borotungstate.[12]

Certain compounds produced by the action of an electric current on a mixture of alkali tungstates with alkaline earth tungstates, and known as tungsten bronzes, have been described. Potassio-calcium bronze has the formula $CaW_4O_{12}.5K_2W_4O_{12}$, and the sodio-calcium bronzes, $CaW_4O_{12}.5Na_2W_5O_{15}$ and $CaW_4O_{12}.10Na_2W_3O_9$.[3]

A calcium sodium paratungstate, $3Na_2O.2CaO.12WO_3.34H_2O$, is also known [11]

Mazzucchelli and Inghilleri described a complex pertungstate to which they gave the name calcium ozo-tungsto-oxalate, $CaC_2O_4.WO_4.H_2O$. They obtained it by the action of hydrogen peroxide on calcium tungsto-oxalate which is prepared by the action of calcium chloride on the corresponding potassium salt.[15]

CALCIUM AND URANIUM.

Calcium Uranate, $CaUO_4$, may be obtained by fusing calcium chloride with green uranium oxide, U_3O_8,[16] and the diuranate, CaU_2O_7, by heating with fused calcium or sodium chloride, the amorphous uranate prepared by acting upon uranium oxide with calcium chlorate.

Calcium Peruranate, $(CaO_2)_2.UO_4.10H_2O$, is formed as a bright yellow crystalline precipitate by the action of calcium chloride on the

[1] Saint-Sernin, *Compt. rend*, 1913, 156, 1019 ; de Schulten, *Bull. Soc. min. de France*, 1903 26, 112; Lefort, *Ann. Chim. Phys*, 1878, [5], 15, 32

[2] Manross, *loc. cit.*; Zambonini, *Zeitsch. Kryst. Min.*, 1906, 41, 53 ; de Schulten, *loc. cit.*, found the density of the precipitated salt to be 5·542.

[3] Lefort, *loc. cit.*

[4] Hodgson, *Phys. Review*, 1918, [2], 12, 431.

[5] Kopp, *Annalen Suppl.*, 1864–5, 3, 296.

[6] von Knorre, *Ber.*, 1885, 18, 326.

[7] Lefort, *Ann. Chim. Phys.*, 1879, [5], 17, 470.

[8] Scheibler, *J. prakt. Chem.*, 1860, [1], 80, 204 ; 1861, [1], 83, 273 ; Wyrouboff, *Bull. Soc. franç. Min.*, 1892, 15, 63.

[9] Gibbs, *Amer. Chem. J.*, 1885–6, 7, 392 ; Péchard, *Compt. rend.*, 1890, 110, 754 ; *Ann. Chim. Phys.*, 1891, [6], 22, 233.

[10] Marignac, *Ann. Chim. Phys.*, 1864, [4], 3, 5.

[11] Kehrmann, *Annalen*, 1889, 245, 45.

[12] Klein, *Ann. Chim. Phys.*, 1883, [5], 28, 350.

[13] Engels, *Zeitsch. anorg. Chem*, 1903, 37, 125.

[14] Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 44.

[15] Mazzucchelli and Inghilleri, *Atti R. Accad. Lincei*, 1908, [5], 17, ii., 30.

[16] Ditte, *Compt. rend.*, 1882, 95, 988, see *Jahresber.*, 1882, 230.

corresponding sodium salt. It belongs to the rhombic system. With sulphuric acid hydrogen peroxide is formed.[1]

CALCIUM AND NITROGEN.

Calcium Nitride, Ca_3N_2, in an impure state was first obtained by Maquenne by heating calcium amalgam in a current of nitrogen.[2]

Moissan prepared it as small, transparent, yellow-brown crystals, of density 2·63 at 17° C., by heating calcium in a nickel boat in a current of nitrogen.[3] "Active" calcium,[4] produced by melting and then cooling slowly to form a coarse-grained crystalline structure, begins to absorb nitrogen at 300° C. The maximum action is at 440° C., above which temperature the rate slows down until it ceases at 800° C. The absorption is favoured by the presence of a superficial layer of nitride. By quickly chilling metallic calcium from 840° C. an " inactive " form is produced which only begins to combine with nitrogen at 800° C. " Active " calcium produces a brown nitride, and " inactive " black. The velocity is expressed by the formula $v = K \sqrt[3]{P^2}$ where v is the velocity, P the pressure of nitrogen, and K a constant.

Pure calcium is almost passive towards nitrogen, but the presence of more electropositive metals, for example, potassium and barium, accelerates the absorption, arsenic and antimony retard it, and bismuth, copper, and zinc apparently protect it completely. Calcium nitride always acts as an accelerator. With a suitable alloy, containing also 5 per cent. of nitride, pure argon can be obtained in a few minutes from atmospheric nitrogen, even below 320° C.[5]

The melting-point of calcium nitride is about 1200° C.[3] It reacts with chlorine and bromine vapour in the cold, or with only a slight rise in temperature, with iodine vapour at dull red heat, with phosphorus and sulphur at red heat, and with carbon in the electric furnace, forming carbide, the cyanide being an intermediate product. Water attacks it immediately, giving calcium hydroxide and ammonia. With dilute acids it forms calcium and ammonium salts, but is not affected by concentrated sulphuric and nitric acids. Alcohol reacts with it at red heat, forming the ethylate and ammonia. Sodium, potassium, and magnesium have no effect upon it at red heat. When heated strongly in hydrogen, calcium hydride, nitrogen, and some ammonia are formed. The reaction is reversible, according to Haber and van Oordt.[6] Ammonia is not formed in the reverse reaction.

$$Ca_3N_2 + 3H_2 \rightleftharpoons 3CaH_2 + N_2.$$
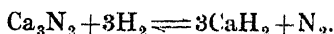
Moissan proposed the use of calcium nitride as an intermediary in the fixation of atmospheric nitrogen.

[1] Melikoff and Pissarjewski, *Ber.*, 1897, **30**, 2902.

[2] Maquenne, *Bull. Soc. chim.*, 1892, [3], **7**, 366; *Compt. rend.*, 1892, **114**, 25; *Ann. Chim. Phys.*, 1893, [6], **29**, 215; see also Férée, *Compt. rend.*, 1898, **127**, 618.

[3] Moissan, *Compt. rend.*, 1898, **127**, 497.

[4] Sieverts, *Zeitsch. Elektrochem.*, 1916, **22**, 15; see also Brandt, *Zeitsch angew. Chem.*, 1914, **27**, 424. See p. 16.

[5] Ruff, *Zeitsch. physikal. Chem.*, 1922, **100**, 419; Ruff and Hartmann, *Zeitsch. anorg. Chem.*, 1922, **121**, 167.

[6] Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1905, **44**, 341; see also Reid and Serpek, *Helv. Chim. Acta*, 1920, **3**, 138.

The heat of formation of calcium nitride is 111·2 Cal.[1]

Calcium Azide, $Ca(N_3)_2$, is obtained by treating lime with a dilute solution of hydrazoic acid, and evaporating over sulphuric acid, or by boiling freshly precipitated calcium hydroxide in excess with a solution of ammonium azide.[2] It forms small, white, hemispherical aggregates of rhombic crystals which explode violently on heating, but not by shock,[3] the explosion temperature being 158° C.;[4] nitrogen is evolved and metallic calcium remains.

It is hygroscopic, readily soluble in water, and isomorphous with barium and strontium azides.

Tiede suggested that the azides of the alkalies and the alkaline earths might be used for the preparation of pure nitrogen by decomposing them in a Gaede vacuum. The temperature at which the evolution of nitrogen from calcium azide begins under these conditions is 110° C., but 100° C. is then sufficient to maintain the reaction.[5]

Calcium azide is very soluble in water, 100 parts dissolving 38·1 parts of the salt at 0° C., and 45·0 parts at 15·2° C. It is only slightly soluble in absolute alcohol and insoluble in ether. The aqueous solution can be evaporated without change.[2]

Calcium Ammonium, or Calcium Hexammoniate, $Ca(NH_3)_6$.— Metallic calcium dissolves in liquid ammonia, forming a blue solution. On passing ammonia over metallic calcium at 15°–20° C. heat is evolved, and a bronze-coloured solid, which takes fire in air, is left. Moissan gave to it the formula $Ca(NH_3)_4$.[6]

Kraus studied the vapour pressure of the system calcium : ammonia.[7] Two liquid phases in contact with one another may be obtained. At −33° C. the dilute phase did not exceed $\frac{1}{10}$ gram-atom per litre, whilst the concentrated phase had a metallic reflection. The form of the vapour pressure curve indicated the presence of only one compound and that had a composition $Ca(NH_3)_6$.

By heating under reduced pressure, Botolfsen observed explosive decomposition which he ascribed to an unstable ammoniate of composition $Ca_2(NH_3)$, and he suggested the existence of a series of ammonium compounds.[8]

The following values for the dissociation pressures of the hexammoniate have been found [9] :—

Temperature, ° C.	−11	12	44
Pressure in mm. mercury	17·5	50	307

The heat of formation calculated from these dissociation pressures is 10·32 Cal.[10]

Calcium hexammoniate exhibits metallic electrical conduction, as

[1] de Forcrand, *Ann. Chim. Phys.*, 1911, [8], **24**, 256 ; Guntz and Bassett found 112·2 Cal., *Compt. rend* , 1905, **140**, 863.

[2] Curtius and Rissom, *J. prakt Chem.*, 1898, [2], **58**, 285.

[3] Dennis and Benedict, *J. Amer. Chem Soc.*, 1898, **20**, 225 ; *Zeitsch. anorg. Chem.*, 1898, **17**, 18 ; see also Curtius and Rissom, *loc. cit.*

[4] Wöhler and Martin, *Zeitsch. angew. Chem.*, 1917, **30**, 33.

[5] Tiede, *Ber.*, 1916, **49**, 1742.

[6] Moissan, *Compt rend.*, 1898, **127**, 685 ; 1901, **133**, 715.

[7] Kraus, *J. Amer. Chem. Soc.*, 1908, **30**, 653.

[8] Botolfsen, *Ann. Chim.*, 1922, [9], **18**, 1.

[9] Biltz and Hüttig, *Zeitsch. anorg. Chem.*, 1920, **114**, 241 ; Biltz, *Zeitsch. Elektrochem.*, 1920, **26**, 374.

[10] See also Kraus, *loc. cit.*

also does the liquid from which it is precipitated. It is probable that ammonia is combined with the metal in the same way as in ammoniated salts or solvated ions, and that in solution a free positive ion, $Ca(NH_3)_6$, such as is present to some extent when a calcium salt is dissolved in ammonia, and two negative electrons are formed.[1] Gibson and Argo consider that the colour of the solution is due to the combination of the solvent with these electrons.[2]

Acetylene reacts with calcium ammonium at 70° C., giving a compound to which the formula $CaC_2.C_2H_2.4NH_3$ has been ascribed.[3]

Calcium Amide, $Ca(NH_2)_2$.—When calcium ammonium is kept at ordinary temperatures, even in contact with ammonia, it slowly decomposes, giving transparent crystals of calcium amide, $Ca(NH_2)_2$.[4]

By the action of hydrogen on calcium nitride at 300° C., Dafert and Miklauz obtained another amide to which they gave the formula $Ca_3(NH_2)_2$.[5]

A number of substituted amides have been prepared by the action of organic amino-compounds on calcium, for example, calcium anilide, $Ca(C_6H_5NH)_2$, calcium ortho- and para-tolylamide, $Ca(C_7H_7NH)_2$, calcium diphenylamide, $Ca(C_{12}H_{10}N)_2$, and so on.[6]

By the action of potassamide on a calcium salt in ammonia solution a white, amorphous, microcrystalline precipitate is obtained. It is insoluble in liquid ammonia but is dissolved and decomposed by a solution of ammonium nitrate in liquid ammonia, and is hydrolysed by water with the production of calcium hydroxide and ammonia. Franklin regarded it as $CaNK.2NH_3$, and called it potassium ammonocalcate. The formula might also be written as that of a molecular compound of the two amides $Ca(NH_2)_2.KNH_2$.[7] If there is no excess of potassamide, calcium amide only is formed.

Calcium Imide, CaNH, is formed as a greyish-white powder by passing a mixture of hydrogen and nitrogen over heated calcium metal, nitride, or hydride, at 730°-750° C.[5] It is extremely sensitive to light, a few minutes' exposure causing it to turn a dark brown colour owing to the liberation of calcium nitride in accordance with the following equation :—

$$4CaNH = Ca(NH_2)_2 + Ca_3N_2.$$
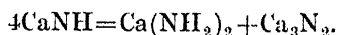
The reaction may be reversed by heat.

By heating *in vacuo*, the imide is again formed and ammonia is split off.

$$Ca(NH_2)_2 = CaNH + NH_3.$$
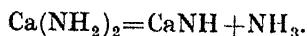
Calcium Hydroxylamite, $Ca(ONH_2)_2$, is formed with the evolution of a gas when calcium filings are treated with anhydrous hydroxylamine at 5° C. An extremely explosive white salt separates. On washing with absolute alcohol and drying *in vacuo* over sulphuric acid, a

[1] Kraus, *loc. cit.* ; *J. Amer. Chem. Soc.*, 1922, 44, 1216.
[2] Gibson and Argo, *ibid.*, 1918, 40, 1327.
[3] Moissan, *Compt. rend.*, 1898, 127, 911.
[4] Moissan, *Ann. Chim. Phys.*, 1899, [7], 18, 289.
[5] Dafert and Miklauz, *Monatsh.*, 1913, 34, 1685.
[6] Erdmann and van der Smissen, *Annalen*, 1908, 361, 33.
[7] Franklin, *J. Amer. Chem. Soc.*, 1915, 37, 2295.

white amorphous powder, detonating at 180° C., is obtained. Water hydrolyses it, forming calcium hydroxide and hydroxylamine.[1]

By digesting calcium hydroxide or carbide with a methyl alcoholic solution of hydroxylamine a basic compound, CaOH.ONH$_2$, is formed.[2] It is a white substance decomposed by water and acids.

Calcium Imidosulphonate, Ca$_3$N$_2$(SO$_3$)$_4$, obtained by treating pure calcium hydroxide with a solution of diammonium imidosulphonate, has been described.[3] It forms transparent crystals probably containing 10 molecules of water of crystallisation. There is also a calcium sodium imidosulphonate, CaNaN(SO$_3$)$_2$.3H$_2$O, and a calcium ammonium and a soluble acid calcium salt which have not been analysed.

Calcium Hyponitrite, CaN$_2$O$_2$.4H$_2$O, is obtained by the action of silver hyponitrite,[4] or sodium hyponitrite,[5] on calcium chloride. It is crystalline and stable at ordinary temperatures, but at 100° C. gives up water with partial decomposition. It is not very soluble in water. Sulphuric acid decomposes it with effervescence. Most oxidising agents, such as bromine, iodine, chromic acid, and hypobromites, react very vigorously with it, but potassium permanganate reacts only slowly. It dissolves in acetic acid at temperatures between 30° and 100° C., forming an unstable crystalline compound, soluble in water, to which Maquenne ascribed the formula

$$CaN_2O_2.Ca(CH_3COO)_2.2CH_3COOH.4H_2O.$$
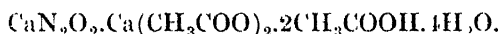
Calcium Nitrohydroxylaminate, CaN$_2$O$_3$.3½H$_2$O, is prepared by the action of the corresponding sodium salt on calcium chloride solution. It forms transparent crystals only slightly soluble in water, and decomposed by mineral acids and acetic acid. On heating to 125° C. it loses 3 molecules of water, and at a still higher temperature breaks up into a mixture of nitrite and hyponitrite.[6] It is also decomposed by mineral acids and by acetic acid.

Calcium Nitrite, Ca(NO$_2$)$_2$, may be obtained by careful calcination of the nitrate, with or without a reducing agent,[7] but this is not satisfactory owing to the fact that the temperature at which decomposition of the nitrate commences is 500° C., whereas for the nitrite it is 220° C. It may also be prepared in solution by the action of silver nitrite on calcium chloride.[8] From this it crystallises in very faintly yellow hexagonal needles[9] which contain 1 molecule of water of crystallisation and are isomorphous with barium and strontium nitrites.

Dehydration over sulphuric acid appears to result in the formation of a half-hydrate, Ca(NO$_2$)$_2$.½H$_2$O,[9] and Oswald[10] obtained a tetrahydrate Ca(NO$_2$)$_2$.4H$_2$O, of density 1·674 at 0° C. The hydrated

[1] Ebler and Schott, *J. prakt. Chem.*, 1908, [2], **78**, 289.

[2] Hofmann and Kohlschutter, *Zeitsch. anorg. Chem.*, 1898, **16**, 463.

[3] Divers and Haga, *Trans. Chem. Soc.*, 1892, **61**, 943; 1896, **69**, 1620; *Chem. News*, 1896, **74**, 269.

[4] Maquenne, *Ann. Chim. Phys.*, 1889, [6], **18**, 556; Kirschner, *Zeitsch. anorg. Chem.*, 1898, **16**, 424.

[5] Divers, *Trans. Chem. Soc.*, 1899, **75**, 117.

[6] Angeli and Angelico, *Gazzetta*, 1900, **30**, i., 593; Angelico and Fanara, *ibid.*, 1901, **31**, ii., 15.

[7] Fischer, *Pogg. Annalen*, 1848, **74**, 115; Lang, *ibid.*, 1863, **118**, 281; Hampe, *Annalen*, 1863, **125**, 341; but see Oswald, *Ann. Chim.*, 1914, [9], **1**, 32.

[8] Vogel, *Zeitsch. anorg. Chem.*, 1903, **35**, 385; Oswald, *loc. cit.*

[9] Rây, *Trans. Chem. Soc.*, 1905, **87**, 177.

[10] Oswald, *loc. cit.*

nitrite can be dehydrated *in vacuo* over phosphorus pentoxide without decomposition. The concentrated aqueous solution undergoes hydrolysis at 100° C., but neither the solid nitrite nor the saturated solution is oxidised by oxygen at atmospheric pressure. Oxidation only occurs in the presence of acids, and is then due to the oxidation of the decomposition products of nitrous acid.

Calcium nitrite is very soluble in water, but not in alcohol. A solution saturated at 16° C. contains 42·3 per cent. of nitrite, and has a density of 1·4205.

Oswald studied the system, calcium nitrite: water, from the point of view of the phase rule and obtained the following values for the concentration of the saturated solution of calcium nitrite at different temperatures [1]:—

Temperature, ° C.	Percentage Concentration of Solution.	Solid Phase.
— 4	16·7 ⎫	
— 9·3	25·5 ⎪	
—11 3	28 4 ⎬ . Ice.	
—12·5	29·5 ⎪	
—14·5	32 0 ⎭	
— 9·5	36·2 ⎫	
0	38 3 ⎪	
18·5	43·0 ⎬ . $Ca(NO_2)_2.4H_2O$	
42	51 8 ⎭	
54	55 2 ⎫	
64	58 4 ⎪	
70	60·3 ⎬ . $Ca(NO_2)_2.H_2O$	
73	61 5 ⎪	
91	71·2 ⎭	

The eutectic point is at —17·5° C. at a concentration of 35 per cent. of nitrite. The transition from the tetra- to the mono-hydrate takes place at a temperature of 44 ±2° C., and a concentration of 53·5 ± 1 per cent.

The monohydrate is unchanged in air at ordinary temperatures, and the tetrahydrate effloresces, or is unchanged, according to the pressure of water vapour in the air. Over phosphorus pentoxide, under a pressure of a few centimetres of mercury, the tetra- changes to the monohydrate.

A double nitrite of calcium and cæsium is known, $Cs_2Ca(NO_2)_4.H_2O$,[2] and also one of calcium and mercury, $Hg(NO_2)_2.Ca(NO_2)_2.5H_2O$, which Rây regarded as containing the complex divalent anion $Hg(NO_2)_4''$.[3]

Triple nitrites with potassium and copper have been described.[4]

[1] Oswald, *loc. cit.*
[2] Jamieson, *Amer. Chem. J.*, 1907, **38**, 614.
[3] Rây, *Trans. Chem. Soc.*, 1910, **97**, 326.
[4] Przibylla, *Zeitsch. anorg. Chem.*, 1898, **18**, 148.

Calcium Nitrate, $Ca(NO_3)_2$, does not occur as a mineral form but is often found in natural waters and in the soil as a product of putrefaction and bacterial nitrification. The tetrahydrate forms part of the efflorescence often seen on damp walls, especially on the walls of stables.

It is p~ ~~ed by the neutralisation of calcium hydroxide or calcium carbonate by nitric acid. The anhydrous salt, which may be obtained by drying the hydrated salt at 170° C., is very deliquescent. The melting-point is 499° C.,[1] at which temperature decomposition has already set in to a slight extent.[2] The eutectic mixture of potassium and calcium nitrates, containing 25·36 per cent. of the latter, melts at 251° C.[3]

The heat of formation of anhydrous calcium nitrate from its elements is 216·7 Cal.,[4] and the heat of solution 3·95 Cal.[5] The density is 2·240–2·504.[6] The anhydrous salt crystallises from a hot aqueous or nitric acid solution in microscopic regular octahedra.[7]

Calcium nitrate is very readily soluble in water and tends to form supersaturated solutions. The properties of aqueous calcium nitrate solutions have been extensively investigated with reference to their boiling-points,[8] freezing-points,[9] vapour pressures,[10] densities,[11] refractive indices,[12] viscosities,[13] electrical conductivities,[14] and degree of dissociation.[15] The boiling-point of the saturated solution at 760 mm. pressure is 151° C., and the solution contains 79 per cent. of calcium nitrate.[16]

The Hydrates of Calcium Nitrate.—Calcium nitrate forms several hydrates. The tetrahydrate crystallises from solution at ordinary temperatures in long monoclinic needles.[17] The density is 1·82.[18] The heat of hydration of calcium nitrate is 11·200 Cal., and the heat of solution of the tetrahydrate −7·250 Cal.[19]

From vapour pressure measurements Lescœur concluded that a di- and tri-hydrate probably exist.[20] More recent work has not only confirmed this, but has revealed the existence of a second and unstable

[1] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, [5], **41**, 360; Carnelley found 561°±6° C., *Trans. Chem. Soc.*, 1878, **33**, 273.

[2] Oswald, *loc. cit.*

[3] Guthrie, *Phil. Mag.*, 1884, [5], **17**, 462.

[4] Thomsen, *Thermochemistry*, trans. by Burke (Longmans, Green & Co.), 1908, p. 324.

[5] Thomsen, *loc. cit.*; *J. prakt. Chem.*, 1872, [2], **17**, 165.

[6] Clarke, *Constants of Nature* (Macmillan & Co.), 1888, p. 110; see also Filhol, *Ann. Chim. Phys.*, 1847, [3], **21**, 415; Favre and Valson, *Compt. rend.*, 1875, **77**, 579.

[7] Retgers, *Zeitsch. Kryst. Min.*, 1889, **21**, 257.

[8] Gerlach, *Zeitsch. anal. Chem.*, 1887, **26**, 413

[9] Arrhenius, *Zeitsch. physikal. Chem.*, 1888, **2**, 491; Rudorff, *Pogg. Annalen*, 1861, **114**, 63; Jones and Getman, *Zeitsch. physikal. Chem.*, 1904, **49**, 385.

[10] Wüllner, *Pogg. Annalen*, 1860, **110**, 564; Waddell, *Chem. News*, 1895, **72**, 201.

[11] Gerlach, *Zeitsch. anal. Chem.*, 1888, **27**, 310, 329.

[12] Damien, *Beibl. Wied. Annalen*, 1881, **5**, 579; Jones and Getman, *loc. cit.*

[13] Wagner, *Zeitsch. physikal. Chem.*, 1890, **5**, 31.

[14] Kohlrausch and Gruneisen, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1215; MacGregory, *Wied. Annalen*, 1894, **51**, 126.

[15] Jones and Getman, *loc. cit.*

[16] Bassett and Taylor, *Trans. Chem. Soc.*, 1912, **101**, 576.

[17] Marignac, *Ann. Mines*, 1856, [5], **9**, 1; Millon, *Ann. Chim. Phys.*, 1842, [3], **6**, 73; *Compt. rend.*, 1842, **14**, 905.

[18] Clarke, *loc. cit.*; Filhol, *loc. cit.*

[19] Thomsen, *J. prakt. Chem.*, 1872, [2], **17**, 165.

[20] Lescœur, *Zeitsch. physikal. Chem.*, 1888, **2**, 761; *Ann. Chim. Phys.*, 1890, [6], **21**, 511; see also Millon, *Ann. Chim. Phys.*, 1842, [3], **6**, 90; Gernez, *Compt. rend.*, 1909, **149**, 81.

modification of the tetrahydrate.[1] The nature of the solid phases in contact with saturated solutions of calcium nitrate at different temperatures is indicated by the curves in Fig. 4.[2]

The cryohydric temperature indicated by point A is $-28\cdot7°$ C. at a concentration of $42\cdot9$ per cent. of anhydrous salt.

The melting-point of the stable α-tetrahydrate (point B) is $42\cdot7°$ C.,[3] and of the β-form (point B'), $39\cdot6°$ C.

The trihydrate, the stable hydrate between C and E, which forms
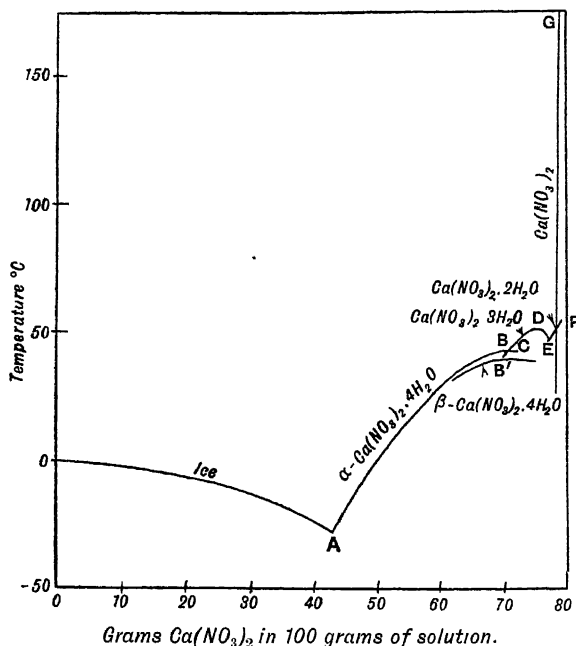
Fig. 4.—Equilibria in the system, calcium nitrate : water.

flattened prismatic crystals apparently belonging to the triclinic system, melts at $51\cdot1°$ C. (point D).

The dihydrate in smaller prismatic crystals has no true melting-point, as can be seen from the diagram where the range of existence is line EF lying between the temperatures $48\cdot4°$ and $51\cdot3°$ C.

As the line FG shows, there is only a very slight increase in the solubility of the anhydrous salt with rise of temperature.

A hexahydrate, $Ca(NO_3)_2.6H_2O$, of melting-point $26\cdot4°$ C., is mentioned by Tilden,[4] but there does not appear to be any confirmatory evidence.

Calcium nitrate, known as " air-saltpetre," is obtained technically

[1] Bassett and Taylor, *Trans. Chem. Soc.*, 1912, **101**, 576; Taylor and Henderson, *J. Amer. Chem. Soc.*, 1915, **37**, 1688; see also Arrhenius, *Zeitsch. physikal. Chem.*, 1888, **2**, 491; Rüdorff, *Pogg. Annalen*, 1861, **114**, 631; Raoult, *Zeitsch. physikal. Chem.*, 1888, **2**, 488; Jones and Getman, *ibid*, 1904, **49**, 385; d'Ans and Siegler, *ibid.*, 1913, **82**, 35.
[2] See Calcium Chloride.
[3] Morgan and Owen, *Zeitsch. anorg. Chem.*, 1908, **56**, 168, obtained $42\cdot31°$ C.
[4] Tilden, *Trans. Chem. Soc.*, 1884, **45**, 266.

in the fixation of atmospheric nitrogen by the arc process, the nitrous gases being absorbed by calcium oxide or calcium carbonate.[1] It is as effective a fertiliser as sodium nitrate, but it has not appeared to any great extent in the English country markets.[2] The difficulties caused by its hygroscopic nature have to some extent been overcome.

The preparation of calcium nitrate on a commercial scale by the bacterial oxidation of calcium cyanamide, or of ammonium compounds in the presence of calcium carbonate, has also been suggested.[3]

A patent has been taken out for neutralising nitric acid with a mixture of rock phosphate and limestone.[4] A hard dry mass of considerable fertilising value is said to be obtained.

Addition Compounds.—Calcium nitrate solutions absorb ammonia more readily than does pure water,[5] evidently as the result of the formation of a complex cation $Ca(NH_3)_n$.

Calcium nitrate is very soluble in ethyl alcohol and forms an alcoholate, $Ca(NO_3)_2.2C_2H_5OH$.[6] It also dissolves readily in methyl, propyl, isobutyl, and amyl alcohols, and in acetone, but not in ether and paracetaldehyde.

Basic Calcium Nitrates.—If calcium hydroxide be added to a saturated solution of calcium nitrate until no more dissolves, the liquid becomes semi-solid after a few minutes and contains crystals of composition $Ca(NO_3)_2.Ca(OH)_2.2.5H_2O$. The compound loses its water of crystallisation at 160° C., and is decomposed by water.[7] Bassett and Taylor gave the formula as $Ca_2N_2O_7.3H_2O$, and stated that at 100° C. the hydrates $Ca_2N_2O_7.2H_2O$ and $Ca_2N_2O_7.0.5H_2O$ may be obtained.[8]

Quicklime, when slaked with a concentrated solution of calcium nitrate, gives white needles of the compound $2Ca(OH)_2.Ca(NO_3)_2.2H_2O$ which become turbid on the addition of water.[9]

CALCIUM AND PHOSPHORUS.

Calcium Phosphide, Ca_3P_2, was first obtained in an impure form, probably contaminated with phosphate, by the action of phosphorus vapour on red-hot lime.[10] Phosphorus and metallic calcium combine directly to give amorphous calcium phosphide.[11]

Moissan obtained a red crystalline phosphide by the reduction of tricalcium phosphate by carbon in the electric furnace.[12] It is a refractory substance only fused in the electric furnace. The density is 2.5 at 15° C. When heated *in vacuo* it slowly decomposes. Hydrogen and nitrogen have no action even at 900° C., nor boron, carbon, sul-

[1] Schönherr, *Trans. Amer. Electrochem. Soc.*, 1909, 16, 131.

[2] Russell, *J. Soc. Chem. Ind.*, 1917, 36, 250 ; *App. Chem. Reports*, 1919, 4, 368.

[3] Thorsell and Lundén, British Patents, 131493, 132625, 132882, 132883 (1918), see *Chem. Abs.*, 1920, 14, 319.

[4] Howorth, English Patent, 114873 (1917), see *J. Soc. Chem. Ind.*, 1918, 37, 315A.

[5] Raoult, *Ann. Chim. Phys.*, 1874, [5], 1, 270.

[6] d'Ans and Siegler, *Zeitsch. physikal. Chem.*, 1913, 82, 35.

[7] Werner, *Ann. Chim. Phys*, 1892, [6], 27, 570 ; *Compt. rend.*, 1892, 115, 169 ; Cameron and Robinson, *J. Physical Chem.*, 1907, 11, 273.

[8] Bassett and Taylor, *Trans. Chem. Soc.*, 1914, 105, 1926.

[9] Busvold, *Zeitsch. anorg. Chem.*, 1916, 98, 202.

[10] Thénard, *Ann. Chim. Phys.*, 1845, [3], 14, 5.

[11] Moissan, *ibid.*, 1899, [7], 18, 289.

[12] Moissan, *Compt. rend*, 1899, 128, 787 ; *Electric Furnace*, English translation by Monlpied (Williams & Norgate), 1904, p. 281; see also Rénault, *Compt. rend.*, 1899, 128, 883.

phuretted hydrogen, and ammonia at 700° C., but in the electric furnace phosphorus is replaced by carbon. Calcium phosphide is decomposed at once by water and dilute acids, giving phosphoretted hydrogen, but not by concentrated nitric and sulphuric acids in the cold. It burns brilliantly in oxygen at 300° C., giving lime and phosphorus pentoxide. Sulphur also reacts at 300° C. with considerable evolution of heat. Chlorine and bromine react vigorously at 100° C., and iodine at red heat, as also do the halogen acids in the gaseous state. There is a vigorous reaction with incandescence when the phosphide is heated with an oxidising agent such as potassium chlorate, dichromate, or permanganate. Absolute alcohol, ether, benzene, and turpentine have no action at ordinary temperatures.

Ignition of an intimate mixture of calcium phosphate and aluminium powder affords a rapid method for obtaining a source of phosphorus trihydride which is not spontaneously inflammable, and is only contaminated with a little hydrogen.[1]

Calcium Dihydrohypophosphite, $Ca(H_2PO_2)_2$, is obtained by the action of phosphorus on boiling milk of lime,[2] or of water on the phosphide.[3] It forms anhydrous hexagonal monoclinic crystals, easily soluble in water, 1 part of salt to 6 of water, but insoluble in alcohol and unchanged by heat below 300° C. Above that temperature it is decomposed with loss of water and phosphoretted hydrogen, and formation of calcium pyro- and meta-phosphate,[4] in the molecular proportions of 3 to 1.

It is employed in therapeutics.

Two double salts are known, a calcium cobalt hypophosphite, $Ca_2Co(H_2PO_2)_6.2H_2O$, forming efflorescent red octahedral crystals, and a calcium cadmium salt, which may, however, be a mixture.[5]

Calcium Hydrophosphite, $CaHPO_3$, or neutral calcium phosphite, is obtained as a white crystalline powder by precipitating calcium chloride with ammonium phosphite.[6] The crystals have the composition $H_4Ca_2P_2O_7.2H_2O$ or $2CaHPO_3.2H_2O$, and lose 1 molecule of water at 100° C. and the rest between 200° and 300° C.[7] The dry salt is decomposed at red heat and the solution on boiling.

Calcium Dihydrophosphite, $Ca(H_2PO_3)_2$, or Acid Calcium Phosphite.—By dissolving calcium carbonate in phosphorous acid, in the proportion of 1 molecule of the former to 2 of the latter, and evaporating *in vacuo*, a crystalline compound of the composition $Ca(H_2PO_3)_2.H_2O$ is obtained.[8] It loses its water of crystallisation above 150° C. It is very readily soluble in water and from the solution alcohol precipitates the neutral salt.

By dehydrating the acid phosphite between 145° and 170° C., calcium pyrophosphite, $CaH_2P_2O_5$, may be prepared.[9]

[1] Matignon and Trannoy, *Compt. rend.*, 1909, **148**, 167.
[2] Rose, *Pogg. Annalen*, 1827, **9**, 364; Engelhardt, *Jahresber.*, 1860, 70; Berlandt, *Arch. Pharm.*, 1865, [2], **122**, 237; Wurtz, *Ann. Chim. Phys.*, 1843, [3], **7**, 35.
[3] Wurtz, *Annalen*, 1842, **43**, 318.
[4] Rammelsberg, *Ber.*, 1872, **5**, 492; *Sitzungsber. K. Akad. Wiss. Berlin*, 1872, 409, see *Jahresber.*, 1872, 208; Rose, *loc. cit.*
[5] Abegg, *Handbuch d. anorg. Chem.* (S. Hirzel, Leipzig), 1907, III. Bd., **3** Abt., p. 431.
[6] Rose, *Pogg. Annalen*, 1827, **9**, 26.
[7] Rammelsberg, *Jahresber.*, 1866, 115; *Pogg. Annalen*, 1867, **131**, 263; *Ber.*, 1868, 1, 186.
[8] Wurtz, *Ann. Chim. Phys.*, 1846, [3], **16**, 190; Amat, *ibid.*, 1891, [6], **24**, 289.
[9] Amat, *loc. cit.*

Neutral Calcium Hypophosphate, $CaPO_3.H_2O$, is obtained as a white gelatinous precipitate, becoming granular on washing, by the interaction of sodium hypophosphate and calcium chloride solutions. It does not crystallise, is insoluble in water, only slightly soluble in acetic acid, but soluble in hydrochloric and hypophosphoric acid. It is dehydrated at 200° C. with partial oxidation.[1]

Acid Calcium Hypophosphate, $CaH_2P_2O_6$, may be prepared by mixing freshly precipitated lime and hypophosphoric acid in exactly equivalent proportions and evaporating in the cold. Heating the solution gives the neutral salt. A solution of the acid salt may also be obtained by dissolving the neutral salt in hypophosphoric acid, or by digesting with water a mixture of acid barium hypophosphate and calcium sulphate in molecular proportions.

It forms monoclinic crystals of composition $CaH_2P_2O_6.6H_2O$, which easily lose 4 molecules of water at the ordinary temperature. The remaining two are removed at 150° C. with partial decomposition. One part of the salt dissolves in 60 of water.[2]

Calcium Orthophosphates.—Three calcium orthophosphates exist and have an extensive literature, which is often contradictory owing to the failure to appreciate the consequences of combining a comparatively strong base with a weak acid. The importance of a careful study of their properties arises from a widespread use of phosphates as fertilisers. Especially is it necessary to examine their behaviour with water. There have been considerable discrepancies between the results of solubility determinations,[3] because the extent of the decomposition of the phosphates by water has not been taken fully into consideration. Both tricalcium and monocalcium phosphates give an acid solution when treated with water,[4] the amount of acid depending on temperature and on the ratio of the mass of the water to the mass of the solid phosphate. In the case of the monocalcium phosphate the dicalcium salt is often precipitated. The latter salt is comparatively little affected,[5] but, by treatment with successive quantities of water, the residue is ultimately transformed, with more or less completeness, into tricalcium phosphate.[6]

In more recent times the ternary system, lime : phosphoric acid : water, has been carefully studied with a view to determining the conditions of stability of the different compounds.[7] The problem is complicated by the following factors : the existence of several different

[1] Salzer, *Annalen*, 1878, **194**, 28

[2] Salzer, *ibid*, 1886, **232**, 114.

[3] Birnbaum and Packard, *Zeitsch. Chem.*, 1871, 137; Dusart and Pelouze, *Compt. rend.*, 1868, **66**, 1327; Causse, *ibid.*, 1892, **114**, 414; *Bull. Soc. chim.*, 1892, [3], **7**, 165; Volcker, *Jahresber.*, 1862, 131; Warington, *J. Chem. Soc.*, 1866, **19**, 296; 1873, **26**, 983; Joffre, *Bull. Soc. chim.*, 1898, [3], **19**, 372; Schlösing, *Compt. rend.*, 1900, **131**, 149; Pollacci, *J. Chem. Soc.*, 1897, **72**, Abs. ii., 260; Maly and Donath, *J. prakt. Chem.*, 1873, [2], **7**, 413; Williams, *Chem. News*, 1871, **24**, 306; Rindell, *Compt. rend.*, 1902, **134**, 112.

[4] Warington, *loc. cit.*; Joly and Sorel, *Compt. rend.*, 1894, **118**, 738; Cameron and Seidell, *J. Amer. Chem. Soc.*, 1904, **26**, 1454; Joly, *Compt. rend.*, 1883, **97**, 1480.

[5] Schlösing, *Compt. rend.*, 1900, **131**, 211; Rindell, *loc. cit.*; Cameron and Seidell, *loc. cit.*; Bell, *J. Amer. Chem. Soc.*, 1910, **32**, 879. According to Wendt and Clarke, *J. Amer. Chem. Soc.*, 1923, **45**, 881, the dicalcium phosphate is the least stable of the three. See also Jolibois, *Compt. rend.*, 1919, **169**, 1161.

[6] Buch, *Zeitsch. anorg. Chem.*, 1907, **52**, 325.

[7] Cameron and Seidell, *J. Amer. Chem. Soc.*, 1905, **27**, 1503; Cameron and Bell, *ibid.*, 1910, **32**, 869; Bassett, jun., *Proc. Chem. Soc.*, 1906, **22**, 315; *Zeitsch. anorg. Chem.*, 1907, **53**, 34; *Trans. Chem. Soc.*, 1917, **111**, 620.

hydrates, the precipitation of the phosphates in both gelatinous and crystalline forms, and the slowness with which equilibrium is established. Bassett[1] determined three quintuple points and formulated the changes taking place at these points by the following equations, the portions in brackets indicating the composition of the solutions in contact with the solid phases :—

At 21° C., $CaHPO_4.2H_2O + 0.138CaH_4(PO_4)_2.H_2O = 1.0747CaHPO_4$
$$+ (2.374H_2O + 0.10007P_2O_5 + 0.0627CaO).$$

At 36° C., $CaHPO_4.2H_2O = 0.9985CaHPO_4 + 0.000384Ca_3(PO_4)_2.H_2O$
$$+ (2.00036H_2O + 0.00033CaO + 0.00036P_2O_5).$$

At 152° C., $CaH_4(PO_4)_2.H_2O = 0.495CaH_4(PO_4)_2 + 0.427CaHPO_4$
$$+ (1.80H_2O + 0.292P_2O_5 + 0.078CaO).$$
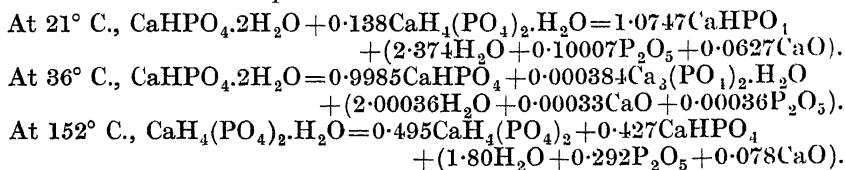
The solubility of the monocalcium phosphate is much greater than that of either of the other two. The phosphates are soluble in all strong acids,[2] and the solubility is considerably increased by the presence of organic acids, for example, acetic, citric, and humic,[3] a fact which has an important bearing on the availability of phosphates in the soil. Addition of phosphoric acid increases the solubility at first, but a very high concentration of acid results in the deposition of monocalcium phosphate.[4] The presence of carbonic[5] or sulphurous[6] acids also makes the phosphates more soluble. Sulphurous acid probably forms a compound with tricalcium phosphate, $3CaO.SO_2.P_2O_5.2H_2O$, consisting of microscopic hexagonal crystals.[7]

Egg albumen increases the solubility,[8] and also most neutral salts except calcium salts.[9] This is especially the case with ammonium salts,[10] probably owing to the formation of complex ions. Potassium chloride and sodium nitrate appear to increase the amount of lime in solution and to decrease the amount of phosphorus pentoxide.[11]

Tricalcium Orthophosphate, $Ca_3(PO_4)_2$, occurs naturally, combined with calcium chloride or fluoride, as the mineral *apatite*. It is also found in layers and nodules in many sedimentary rocks (phosphatic chalk, Florida pebbles, coprolites, etc.). The hills of Christmas Island, and of many other Pacific islands, are capped by layers of pure tricalcium phosphate produced by the action of guano deposits on the coral rocks. There is a large variation in the phosphate content of these sources, which are worked largely for fertiliser. Florida hard rock contains as much as 75–80 per cent. of tricalcium phosphate, the soft sandy deposits of North Africa 57–65 per cent., and the deposits worked in France and Belgium 40–50 per cent. Before the War the production

[1] Bassett, jun., *Zeitsch. anorg. Chem*, 1908, 59, 1.
[2] Crum, *Annalen*, 1847, 63, 394; Baer, *Pogg. Annalen*, 1848, 75, 152.
[3] Rindell, *loc. cit.*; Grupe and Tollens, *Ber.*, 1881, 14, 754; Cameron and Hurst, *J. Amer. Chem. Soc.*, 1904, 26, 885.
[4] Causse, *Bull. Soc. chim.*, 1892, [3], 7, 165.
[5] Dumas, *Compt. rend.*, 1846, 23, 1018; Lassaigne, *ibid.*, 1846, 23, 1019; Joffre, *loc. cit.*; Schlösing, *loc. cit.*; Cameron and Hurst, *loc. cit.*
[6] Gerland, *J. prakt. Chem.*, 1871, [2], 4, 97.
[7] But see Rotondi, *Ber.*, 1882, 15, 1441.
[8] Mercadante, *Gazzetta*, 1875, 5, 311; *Ber.*, 1875, 8, 1357.
[9] Dumas, *loc. cit.*; Lassaigne, *Jahresber.*, 1847 and 1848, 341; Rindell, *loc. cit.*; Cameron and Hurst, *loc cit.*
[10] Grupe and Tollens, *Ber.*, 1880, 13, 1267; Terreil, *Bull. Soc. chim.*, 1881, [2], 35, 548; *Chem. News*, 1881, 44, 66; Barillé, *J. Pharm. Chim*, 1908, [6], 27, 437; Herzfeld and Feuerlein, *Zeitsch. anal. Chem.*, 1881, 20, 191.
[11] Cameron and Hurst, *loc. cit.*

was gradually increasing. The total world production in 1907 was not quite five million long tons, and in 1913 it was over seven million.[1]

Calcium phosphate constitutes the chief part of the mineral matter of teeth and bones, being 50–60 per cent. of the whole, or about 85 per cent. of the ash.[2] A deficiency in phosphates results in diseased or rachitic bones.[3] Milk also contains calcium phosphate.

Calcium phosphate, along with basic phosphates, is a by-product of the basic Bessemer process.[4]

It is obtained as a white gelatinous precipitate by the action of excess of lime on phosphoric acid solution,[5] or by the precipitation of a calcium salt by a tertiary alkali phosphate, or by an acid phosphate in ammonia solution.[6] On drying, an amorphous powder is produced containing varying quantities of water, 1 molecule,[7] 2 molecules,[8] 5 or $5\frac{1}{2}$ molecules.[9]

The melting-point is 1670° C.[10]

If calcium phosphate is heated to 1200° C. with silica and carbon calcium silicate and phosphorus are obtained.[11] This reaction is the basis of a commercial method for the production of phosphorus.[12]

A colloidal solution of calcium phosphate can be prepared by adding slowly, and with continuous shaking, a hot normal solution of calcium chloride containing a definite amount of protective colloid—for example, gelatine, gum arabic, blood serum, or starch. It can also be obtained by the action of a solution of orthophosphoric acid on a solution of calcium hydroxide containing gelatine.[13] It forms an opaque solution, bluish-white by reflected light, and might prove of value in therapeutics.

A sample of calcium phosphate, showing the optical phenomena associated with liquid crystals, has been obtained.[14]

Halogen Compounds of Tricalcium Orthophosphate.—Apatite, $3Ca_3(PO_4)_2 \cdot Ca(Cl,F)_2$, analogous with the natural mineral form, can be prepared artificially by the action of calcium phosphate on a mixture of calcium fluoride and chloride with a little ammonium chloride at red heat. On treatment with water, crystals in the form of regular hexagonal prisms are isolated.[15] Fluorapatite,[16] chlorapatite,[17] and brom-

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[1] Packard, *J. Soc. Chem. Ind.*, 1921, 40, 288R.

[2] Aeby, *J. prakt. Chem.*, 1872, [2], 5, 308; 1873, [2], 6, 169; Wibel, *ibid.*, 1874, [2], 9, 113.

[3] Schloss and Frank, *Biochem. Zeitsch.*, 1914, 60, 378; Weiser, *ibid.*, 1914, 66, 95.

[4] Thomas, *Chem. Zentr.*, 1881, 661; *Jahresber.*, 1881, 1243.

[5] Berthelot, *Ann. Chim. Phys.*, 1887, [6], 11, 350; Schlösing, *Compt. rend.*, 1900, 131, 149.

[6] Cornelis, *J. Pharm. Chim.*, 1886, [5], 13, 29; see also Bassett, jun., *Zeitsch. anorg. Chem.*, 1907, 53, 49.

[7] Schlösing, *loc. cit.*

[8] Warington, *J. Chem. Soc.*, 1866, 19, 296.

[9] Ludwig, *Arch. Pharm.*, 1852, [2], 69, 286.

[10] Dieckmann and Houdremont, *Zeitsch. anorg. Chem.*, 1921, 120, 136, but see Nielsen, *Ferrum*, 1913, 10, 97, see *J. Chem. Soc.*, 1913, 104, Abs. ii., 407.

[11] Berthier, *Ann. Chim. Phys.*, 1826, [2], 33, 154.

[12] See *J. Soc. Chem. Ind.*, 1917, 36, 134.

[13] de Toni, *Kolloid-Zeitsch.*, 1921, 28, 145.

[14] Gaubert, *Compt. rend.*, 1922, 174, 1115.

[15] Deville and Caron, *Ann. Chim. Phys.*, 1863, [3], 67, 443.

[16] Ditte, *ibid.*, 1886, [6], 8, 502; Dieckmann and Houdremont, *Zeitsch. anorg. Chem.*, 1921, 120, 145.

[17] Daubrée, *Compt. rend.*, 1851, 32, 625; *Ann. Mines*, 1851, [4], 19, 654; see *Annalen*, 1854, 80, 222; Briegleb, *ibid.*, 1856, 97, 95; Forchammer, *ibid.*, 1854, 90, 77; Debray, *Ann. Chim. Phys.*, 1861, [3], 61, 419.

apatite,[1] containing only one halogen each, have been prepared. Bassett regards the apatites as complex compounds in which the chlorine is united directly with the phosphorus.[2] This view seems to be justified by the existence of a compound of calcium oxide with phosphorus oxychloride, $CaO.2POCl_3$, which may be regarded as a halogen derivative of $CaO.2PO(OH)_3$, or $CaH_4P_2O_8.H_2O$.[3]

Other chloro- and bromo-phosphates, of composition $Ca_3(PO_4)_2.CaCl_2$,[4] and $Ca_3(PO_4)_2.CaBr_2$,[5] have been obtained.

Dicalcium Orthophosphate, $CaHPO_4$, is found naturally as the mineral *monetite*, combined with 2 molecules of water of crystallisation as the mineral *brushite*,[6] and also as *metabrushite*.[7] It is also present in teak wood,[8] and forms the chief constituent of stone separating in certain diseases of the kidneys.[9]

It is obtained by precipitating an acid solution of a calcium salt with neutral sodium phosphate,[10] or by the action of water on monocalcium phosphate,[11] or of an acid on tricalcium phosphate. Artificial brushite of density 2·317 may be obtained by concentration of a solution of the precipitated phosphate in 25 per cent. acetic acid,[12] and monetite by heating together brushite and water in a closed tube at 150° C.

Whether the dicalcium salt is obtained in orthorhombic crystals combined with 2 molecules of water of crystallisation,[13] or whether it is anhydrous, depends on the conditions of preparation. Precipitated at 100° C., or by alcohol, or from concentrated solutions at lower temperatures, it is anhydrous.[14] At 25° C. the stable solid phase in contact with solutions of concentrations up to 15 per cent. phosphorus pentoxide is $CaHPO_4.2H_2O$.[15] According to Quartaroli,[16] there are two different forms of the dihydrate, one amorphous and the other crystalline, and possessing different chemical properties.

Other hydrates have been mentioned,[17] but they probably do not exist as single chemical individuals.

By the combined action of water on dicalcium phosphate, microscopic crystals are obtained which appear to have the composition $8CaHPO_4.Ca_3(PO_4)_2.2H_2O$.[18] A phosphate of composition $P_2O_5.2CaO.P_2O_5.3CaO.10H_2O$ crystallises from solutions containing

[1] Ditte, *loc. cit.* ; *Compt. rend.*, 1883, **96**, 575.
[2] Bassett, jun., *Trans. Chem. Soc.*, 1917, **iii**, 620.
[3] Bassett and Taylor, *ibid.*, 1911, **99**, 1402.
[4] Deville and Caron, *loc. cit.*
[5] Ditte, *loc. cit.*
[6] Moore, *Amer. J. Sci.*, 1865, [2], **39**, 43, see *Jahresber.*, 1865, 908.
[7] Julien, *Amer. J. Sci.*, 1865, [2], **40**, 367 ; the existence of metabrushite is doubtful, see Bassett, jun., *Zeitsch. anorg. Chem.*, 1907, **53**, 34.
[8] Abel, *J. Chem. Soc.*, 1862, **15**, 91.
[9] Wohler, *Annalen*, 1844, **51**, 437.
[10] Drevermann, *ibid.*, 1853, **87**, 120 ; Vohl, *ibid.*, 1853, **88**, 114.
[11] Erlenmeyer, *Jahresber.*, 1873, 254 ; Joly, *Compt. rend.*, 1883, **97**, 1480.
[12] de Schulten, *Bull. Soc. franç. Min.*, 1903, **26**, 11.
[13] Stein, *Annalen*, 1877, **187**, 79.
[14] Debray, *loc. cit.*
[15] Cameron and Bell, *J. Amer. Chem. Soc*, 1910, **32**, 869.
[16] Quartaroli, *Chem. Abs.*, 1921, **15**, 916.
[17] Dusart and Pelouze, *Compt. rend.*, 1868, **66**, 1327 ; Baer, *Pogg. Annalen*, 1848, **75**, 152 ; Skey, *Chem. News*, 1870, **22**, 61 ; Vorbringer, *Zeitsch. anal. Chem.*, 1870, **9**, 457 ; Raewsky, *Compt. rend.*, 1847, **25**, 205 ; Julien, *Amer. J. Sci.*, 1865, [2], **40**, 367 ; Bassett, jun., *Zeitsch. anorg. Chem.*, 1907, **53**, 34 ; 1908, **59**, 1.
[18] Joly and Sorel, *Compt. rend.*, 1894, **118**, 738.

0·375–0·870 grm. of phosphorus pentoxide per litre in the state of monocalcium phosphate.[1]

Monocalcium Orthophosphate, $Ca(H_2PO_4)_2.H_2O$, has been found in a phosphatic rock in Algeria.[2] It can be obtained by evaporation of a solution of di- or tri-calcium phosphate in phosphoric acid.[3] It crystallises with 1 molecule of water in orthorhombic plates of density 2·02.[4] When pure it is unaffected by exposure to the air, but it is often hygroscopic through contamination with phosphoric acid. In order that this salt may be the stable phase in contact with solutions at 25° C., the latter must contain more than 317 grm. of phosphorus pentoxide per litre.[5]

When heated, the crystallised salt melts at 152° C.[6] If it is allowed to lose water it is transformed into the metaphosphate.[7] By slowly raising the temperature to 170°–180° C., pouring off the clear liquid after a short time, cooling the residue, and finally washing with acetone, triclinic crystals of anhydrous monocalcium phosphate are obtained.[6] It may also be prepared by crystallisation at 160° C. from a solution of calcium carbonate in orthophosphoric acid if the ratio P_2O_5/CaO be sufficiently large. The optimum value is 4 6. If it is less than 3 the monohydrate separates. According to Spring,[8] pressure causes the transformation of mono- into di-calcium phosphate.

Calcium Pyro- and Meta-phosphates.—Neutral calcium pyrophosphate, $Ca_2P_2O_7$ with $1·5H_2O$ (at 100° C.) or H_2O (at 110° C.),[9] is formed by the neutralisation of calcium hydroxide with pyrophosphoric acid, or the precipitation of calcium chloride by an alkali pyrophosphate.[9] It is soluble in acid but not in water.[10] It melts at 1230° C., and has a density of 3 09.[11]

Acid calcium pyrophosphate, $CaH_2P_2O_7.2H_2O$, is prepared by the action of oxalic acid on the neutral salt. It is soluble in water.[12]

Calcium metaphosphate, $Ca(PO_3)_2$, is obtained as a white powder insoluble in water by heating monocalcium orthophosphate to 316° C.[7]

It melts at 970°–980° C., and, on cooling, forms a glass which is difficult to crystallise. The density of the crystalline compound is 2·82, and of the amorphous 2 65.[11]

A hydrated compound, dicalcium metaphosphate, $Ca_2(PO_3)_4.4H_2O$,[13] is formed by precipitating an excess of calcium chloride with an alkali metaphosphate.

Calcium hexametaphosphate, $Ca_3P_6O_{18}$, is precipitated, in the form

[1] Jolibois, *Compt. rend.*, 1919, 169, 1161.
[2] Malbot, *Ann. Chim. Phys.*, 1896, [7], 7, 433.
[3] Erlenmeyer, *Jahresber.*, 1857, 145.
[4] Haushofer, *Zeitsch. Kryst. Min.*, 1883, 7, 265.
[5] Cameron and Seidell, *J. Amer. Chem. Soc.*, 1905, 27, 1503.
[6] Bassett, jun., *loc. cit.*
[7] Maddrell, *Annalen*, 1847, 61, 53.
[8] Spring, *Bull. Soc. chim. Belgique*, 1907, 21, 91. See also Bassett, jun., *Proc. Chem. Soc.*, 1906, 22, 315 ; *Zeitsch. anorg. Chem.*, 1907, 53, 49. Compare the effect of pressure on the reversion of superphosphate, p. 97.
[9] Schwarzenberg, *Annalen*, 1848, 65, 143.
[10] Baer, *Pogg. Annalen*, 1848, 75, 152 ; Rose, *ibid.*, 1849, 76, 1 ; Schwarzenberg, *Annalen*, 1848, 65, 133 ; Reynoso, *Compt. rend.* 1852, 34, 795.
[11] Dieckmann and Houdremont, *Zeitsch. anorg. Chem.*, 1921, 120, 129.
[12] Pahl, *Ber.*, 1874, 7, 478.
[13] Fleitmann, *Pogg. Annalen*, 1849, 78, 358 ; *Jahresber.*, 1849, 234.

of oily globules which afterwards stiffen to a tough gelatinous mass, when a concentrated solution of calcium chloride is treated with sodium hexametaphosphate.[1]

Calcium Ultraphosphates.—These compounds might perhaps be regarded as dehydrated acid metaphosphates. Kroll isolated them when studying the constitution of basic slag, and gave to them the following formulæ :—$CaO.3P_2O_5$, $CaO.3P_2O_5.2H_2O$, $2CaO.3P_2O_5$, and a basic compound, $5CaO.3P_2O_5$,[2] the general formula for the acids from which they are derived being $nH_2O.3P_2O_5$.

Calcium Selenophosphate.—Two selenophosphates, $CaHPSeO_3$. $2CaHPO_4.15H_2O$ and $CaHPSeO_3.8H_2O$, in which part of the oxygen is replaced by selenium, have been described.[3]

Double Salts.—Various double phosphates of the alkalies with calcium are known: the orthophosphates, $CaKPO_4$,[4] $CaNaPO_4$ and $Ca_3Na_6(PO_4)_4$,[4] $Ca(NH_4)PO_4.7H_2O$;[5] the pyrophosphates, $CaK_2P_2O_7$[4] and $CaNa_2P_2O_7.4H_2O$;[6] and the metaphosphates, $2Ca(PO_3)_2.2NaPO_3$. $6H_2O$[7] and $Ca(PO_3)_2.2NH_4PO_3.2H_2O$.[8]

A uranium calcium phosphate, $UO_2.CaO.P_2O_5$,[9] and a thorium calcium phosphate, $ThO_2.CaO.P_2O_5$,[10] have been isolated, and there is a natural calcium manganese phosphate, *fairfieldite*, $(Ca,Mn)_3(PO_4)_2$,[11] and also a natural calcium uranyl phosphate, *autunite*, $Ca(UO_2)_2(PO_4)_2.8H_2O$.[12]

Basic Calcium Phosphates.—Basic slag is supposed to contain tetracalcium phosphate, $4CaO.P_2O_5$,[13] of melting-point $1630°$ C.[14] Kroll regarded it as a basic ultraphosphate, $12CaO.3P_2O_5$.

By heating tricalcium phosphate to $540°$ C., oxyapatite, $3Ca_3P_2O_8.CaO$, is formed. It crystallises in doubly refracting needles of melting-point $1540°$ C. and density 2.99. It is also obtained when tetracalcium phosphate is heated for some time at $1000°$ C., or is treated with boiling water.[15]

According to Bassett,[16] the solid existing in stable equilibrium at $25°$ C., with solutions of a range from faintly acid to nearly pure lime-water, is oxy- or hydroxy-apatite, but, although its composition may be indicated by the formula $3Ca_3(PO_4)_2.Ca(OH)_2$, it is not to be regarded as a basic salt, but rather as the salt of a polymeride of phosphoric acid, $H_{11}P_3O_{13}$ (or $3H_3PO_4.H_2O$), with one hydrogen atom un-neutralised.[17]

[1] Ludert, *Zeitsch. anorg. Chem.*, 1894, **5**, 34.

[2] Kroll, *ibid*, 1912, **76**, 387 ; see also Schwarz, *ibid.*, 1895, **9**, 264.

[3] Ephraim and Majler, *Ber.*, 1910, **43**, 277.

[4] Ouvrard, *Compt. rend.*, 1888, **106**, 1599 ; *Ann. Chim. Phys.*, 1889, [6], **16**, 289 ; Grandeau, *Ann. Chim. Phys.*, 1886, [6], **8**, 193.

[5] Lasne, *Bull. Soc. chim.*, 1902, [3], **27**, 131.

[6] See Abegg, *Handbuch d. anorg. Chem.* (S. Hirzel, Leipzig), 1907, III. Bd., 3 Abt., p. 446.

[7] Lindbom, *Ber.*, 1875, **8**, 122. See also Rose, *Jahresber.*, 1849, 232.

[8] Fleitmann, *Jahresber.*, 1849, 234.

[9] Colani, *Ann. Chim. Phys.*, 1907, [8], **12**, 139 ; see also Debray, *ibid.*, 1861, [3], **61**, 419.

[10] Colani, *Compt. rend.*, 1909, **149**, 207.

[11] Brush and Dana, *Amer. J. Sci.*, 1890, [3], **39**, 201.

[12] Szilard, *Le Radium*, 1909, **6**, 233.

[13] Hilgenstock, *Stahl und Eisen*, 1883, **3**, 498 ; 1886, 6, 525, 719 ; 1887, **7**, 557 ; Jensch, *Ber.*, 1886, **19**, 3093 ; Otto, *Chem. Zeit.*, 1887, **11**, 255.

[14] Dieckmann and Houdremont, *Zeitsch. anorg. Chem.*, 1921, **120**, 138 ; but see Steinweg, *Métallurgie*, 1912, **9**, 28.

[15] Dieckmann and Houdremont, *Zeitsch. anorg. Chem.*, 1921, **120**, 129.

[16] Bassett, *Trans. Chem. Soc.*, 1917, **111**, 620.

[17] Compare the relation of orthophosphoric acid, $H_6P_2O_8$ or $H_4P_2O_7.H_2O$, to pyrophosphoric acid, $H_4P_2O_7$.

The slowness of formation of hydroxy-apatite favours the view that it is produced by polymerisation.

Since hydroxy-apatite is the stable phase at the degree of acidity characteristic of animal tissues, it is reasonable to suppose that the phosphate in bones takes this form.[1] This applies also to phosphates in soils where the conditions are such that all phosphatic fertilisers should be ultimately transformed into hydroxy-apatite. Earthy phosphorites and coprolites are no doubt impure mixtures of calcium carbonate with hydroxy-apatite, in which some of the hydroxyl has been replaced by chlorine or fluorine. This explains why, after fine grinding, these minerals may be used as fertilisers without further treatment.

Phosphatic Fertilisers.—The natural tricalcium orthophosphate of either mineral or organic origin has considerable fertilising value when finely ground,[2] but its action is slow owing to its slight solubility. For intensive cultivation, where a quick-acting fertiliser is necessary, a much more soluble product, namely the monocalcium phosphate, must be employed, and this is obtained in superphosphate of lime.

Superphosphate of Lime.—As a result of the experiments of Lawes, who took out a patent in 1842, the manufacture of this compound was first started in England about the year 1845. It consists simply in the treatment of calcium phosphate with sulphuric acid in order to produce a more soluble phosphate, and the reaction is usually expressed by the equation

$$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca(H_2PO_4)_2 + 2CaSO_4,$$
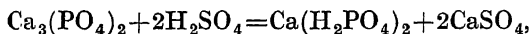
but it is probably more complicated. The presence of a certain amount of free phosphoric acid is necessary to prevent reversion to dicalcium phosphate, and Aita[3] represents the main reaction as follows :—

$$5Ca_3(PO_4)_2 + 11H_2SO_4 = 4CaH_4(PO_4)_2 + 2H_3PO_4 + 11CaSO_4.$$

If properly mixed, the product dries by its own heat of reaction, giving an easily powdered residue. When too large an excess of sulphuric acid is used there is danger of obtaining a sticky mixture which cannot be spread satisfactorily upon the land. With too little sulphuric acid, on the other hand, there is danger of reversion to dicalcium phosphate on keeping, especially if much iron and aluminium are present.[4] Pressure on the lower layers, when the superphosphate is stored in large heaps, also appears to cause reversion.[5]

Superphosphate is tested by its content of water-soluble phosphate, although it is by no means certain that this is a true criterion of its availability to plants.

The system, lime : phosphoric acid : sulphuric acid : water, has been studied by Cameron and Seidell.[6]

It has been suggested that a basic superphosphate, prepared by adding slaked lime to the ordinary superphosphate, might be used for acid soils.[7]

[1] Aeby, *Ber.*, 1874, 7, 555 ; Gabriel, *Zeitsch. physiol. Chem.*, 1894, 18, 257 ; Gassmann, *ibid.*, 1910, 70, 161.
[2] See Hydroxy-apatite.
[3] Aita, *Annali Chim. appl.*, 1918, 10, 45, see *J. Chem. Soc.*, 1919, 116, Abs. ii, 25, and *J. Soc. Chem. Ind*, 1919, 38, 23A.
[4] Shepard, *Chem. News*, 1873, 28, 51 ; Erlenmeyer, *Ber.*, 1881, 14, 1869.
[5] See Monocalcium Orthophosphate, p. 95.
[6] Cameron and Seidell, *J. Amer. Chem. Soc.*, 1906, 28, 1222.
[7] Hughes, *J. Soc. Chem. Ind.*, 1901, 20, 325.

Basic Slag.—Another artificial phosphatic manure is a by-product of the Bessemer process in the iron and steel industry, namely basic or Thomas slag. It was at first regarded as valueless because of the large amount of iron present, until it was shown that the phosphoric acid is all combined with calcium, and is therefore available.[1] The phosphorus is, in fact, apparently more effective than in other phosphatic fertilisers. This may be due to the presence of silica.[2] According to Dieckmann and Houdremont, there should be sufficient silica in basic slag to neutralise any excess of lime above that required for the formation of tricalcium phosphate, and so to form calcium silicophosphate, $Ca_3(PO_4)_2.2CaO.SiO_2$, of melting-point 1760°–1780° C., because this compound, unlike tetra-calcium phosphate, does not decompose during slow cooling to form insoluble oxy-apatite.[3] It is also more soluble than tetraphosphate. Experiments with the finely ground slag began about 1882. Its value was first recognised by the Germans, who manufactured a similar compound, under the name of *Wiborgh Phosphate*, by heating mineral phosphates with soda. It is especially suitable for peaty and clayey soils deficient in lime, and for pasture lands. Its fertilising value is tested by the amount soluble in citric acid solution, but the same criticism applies to this test as to the water-solubility of superphosphate.

In order to reduce slag phosphates to the finely divided state necessary for their efficient utilisation, Plauson's colloidation process, carried out in the presence of small quantities of acid or alkali, may be employed.[4]

Formerly slag manure contained as much as 40 per cent. of phosphate regarded as tricalcium phosphate, but now, owing to the use of the basic open-hearth process, the slag often contains only 20–30 per cent., and it has been suggested that mineral phosphates should be added in the furnace or to the molten slag.[5]

CALCIUM AND ARSENIC.

Calcium Arsenide, Ca_3As_2.—Soubeiran obtained a little arsenide mixed with arsenite by passing arsenic vapour and hydrogen over heated quicklime.[6] It is best prepared by the reduction of calcium arsenate by carbon in the electric furnace,[7] but it may also be formed by the action of liquid arseniuretted hydrogen on metallic calcium or on calcium ammonium,[8] or by the direct combination of calcium and arsenic.[9]

[1] See Basic Calcium Phosphates, p. 96.

[2] Hall and Morison, *Proc. Roy. Soc.*, 1906, **77B**, 455.

[3] Dieckmann and Houdremont, *Zeitsch. anorg. Chem.*, 1921, **120**, 129; see also Blome, *Stahl u. Eisen*, 1910, **30**, 2161.

[4] Plauson, English Patent, 156124, see *Chem. Age*, 1922, **7**, 494.

[5] *J. Ministry Agric.*, 1921, **28**, 521, see *Chem. Abs.*, 1922, **16**, 309. For further details on phosphatic manures see Russell, *Appl. Chem. Reports*, 1918, **3**, 349; Ewan, *ibid.*, 1919, **4**, 165; Greaves and Carter, *Soil Sci.*, 1919, **7**, 121, see *J. Soc. Chem. Ind.*, 1919, **38**, 690A; Hendrick, *J. Soc. Chem. Ind.*, 1919, **38**, 155R; Fowweather, *ibid*, 1919, **38**, 110T; Packard, *ibid.*, 1921, **40**, 288R, 304R; Martin, *Industrial Chemistry, Inorganic* (Crosby Lockwood & Son), 1917, vol. ii, p. 21; Discussion on Basic Slags, *Trans. Faraday Soc.*, 1921, **16**, Pt. 2, 263.

[6] Soubeiran, *Ann. Chim. Phys.*, 1830, [2], **43**, 407.

[7] Lebeau, *Compt. rend.*, 1899, **128**, 95; *Ann. Chim. Phys.*, 1902, [7], **25**, 470; Moissan, *Electric Furnace*, English translation by Monilpied (Williams & Norgate), 1904.

[8] Lebeau, *loc. cit.*

[9] Moissan, *Ann. Chim. Phys.*, 1899, [7], **18**, 289.

It forms a reddish-brown fused mass with a crystalline structure. Its density is 2 5, and in hardness it lies between calcite and glass. It is readily attacked by the halogens, and the higher the atomic weight of the latter the higher the temperature necessary. It remains unchanged in dry air or oxygen, but when heated with oxygen or sulphur, combination readily takes place. With oxidising agents there is a vigorous heat evolution. Hydrogen does not affect the arsenide even at $700°$–$800°$ C. Water decomposes it in the cold with the evolution of arsenuretted hydrogen and formation of calcium hydroxide. Fuming nitric acid does not attack it in the cold, but there is a rapid reaction on heating. Cold concentrated sulphuric acid is reduced to sulphurous acid. Boron and carbon are without action at $1000°$ C., but the latter can decompose it completely at the temperature of the electric furnace. Sulphuretted hydrogen and gaseous halogen acids react at red heat, giving arsenic and a calcium salt. A number of metallic salts are decomposed by the arsenide.

Calcium Arsenites.—The orthoarsenite, $Ca_3As_2O_6$, is obtained as a white amorphous powder by the precipitation of dilute calcium chloride solution with potassium orthoarsenite. The product is dried at $100°$ C.[1] It may also be formed by the precipitation of lime-water with boiling aqueous arsenious acid.[2] It is soluble in acids, but not readily in water. At red heat it is decomposed with volatilisation of arsenic.

The pyroarsenite, $Ca_2As_2O_5$, is a white powder obtained by slowly precipitating a solution of arsenious acid with excess of lime-water, and by heating the precipitate to $105°$ C.[1] A monohydrate has also been described.[3]

Calcium metarsenite, $CaAs_2O_4$, is an amorphous white powder, anhydrous at $100°$ C., obtained by the precipitation of calcium chloride by ammonium arsenite in ammoniacal solution.[1]

A salt of composition $Ca_3As_4O_9.3H_2O$, which may be regarded as consisting of one molecule of pyro- combined with one molecule of metarsenite, has been mentioned.[4]

Calcium Arsenates.—*Tricalcium Orthoarsenate*, $Ca_3(AsO_4)_2$, can be obtained by the action of lime-water on arsenic acid, or by the precipitation of calcium chloride with disodium hydrogen arsenate.[5] A pure product may be prepared by pouring alkaline calcium chloride solution into alkaline sodium hydrogen arsenate.[6] Drying at $100°$ C. gives the dihydrate $Ca_3(AsO_4)_2.2H_2O$. The water of crystallisation is lost at $175°$ C. The density of the dihydrate is $3·23$, and of the anhydrous salt $3·31$. The solubility at $25°$ C. is $0 0133$ grm. per 100 grm. of water.[6]

Calcium arsenate in the form of a spray may be used in place of lead arsenate as an insecticide for plants.[7]

[1] Stavenhagen, *J. prakt. Chem.*, 1895, [2], **51**, 1.
[2] Kühn, *Arch. Pharm.*, 1852, [2], **69**, 267.
[3] Simon, *Pogg. Annalen*, 1837, **40**, 417.
[4] Stein, *Annalen*, 1850, **74**, 218.
[5] Kotschoubey, *J. prakt. Chem.*, 1850, [1], **49**, 182; *Annalen*, 1850, **76**, 249; see also Bloxam, *Chem. News*, 1886, **54**, 193.
[6] Robinson, *J. Agric. Res.*, 1918, **13**, 281, see *J. Soc. Chem. Ind.*, 1918, **37**, 439A.
[7] Robinson, *loc. cit.*; Smith, *J. Amer. Chem. Soc.*, 1920, **42**, 259; Ambruster, *Chem. Met. Eng.*, 1922, **26**, 1155; **27**, 159; but see Pickering, *Proc. Chem. Soc.*, 1907, **23**, 35.

Halogen Compounds of Tricalcium Arsenate.—These are obtained in the same way as the analogous phosphate compounds.[1]

Dicalcium Orthoarsenate, $CaHAsO_4$, is found in nature as the hydrates *pharmacolite,* $CaHAsO_4.2H_2O$, and *haidingerite,* $CaHAsO_4.H_2O$. The densities of the artificially prepared minerals are 2 754 and 2 967 respectively.[2]

The salt may be prepared by treating calcium carbonate with arsenic acid, or by precipitating a soluble calcium salt with disodium hydrogen arsenate.[3] Robinson recommends acidifying both solutions. and states that when dried at 100° C. the compound contains one molecule of water of crystallisation, which it loses before the temperature of 175° C. is reached. The dihydrate may be obtained at ordinary temperatures by slow diffusion.[4] According to Debray[5] and Kotschoubey,[6] there is a hydrate, $2CaHAsO_4.3H_2O$, but this is not confirmed by more recent investigators.[7]

At 25° C. 0 3108 grm. of the anhydrous salt is contained in 100 grm. of the solution.[8]

Monocalcium Orthoarsenate, $CaH_4(AsO_4)_2$, was obtained by Smith during investigations of the system, arsenic pentoxide : calcium oxide : water. At 35° C. it is stable in contact with solutions containing more than 27·5 per cent. of arsenic pentoxide. Below that concentration $CaHAsO_4.H_2O$ is the stable salt.[9]

Calcium Pyroarsenate, $Ca_2As_2O_7$, in orthorhombic prisms, may be obtained by fusing calcium oxide with potassium arsenate.[10] When treated with cold water these break up into minute crystals of the hexahydrate $Ca_2As_2O_7.6H_2O$. By leaving in contact with water the salt is gradually transformed into dicalcium orthoarsenate, $CaHAsO_4.2H_2O$.

Double Salts.—Several double orthoarsenates with the alkalies are known : $CaKAsO_4$, $CaNaAsO_4$, and $Ca_3Na_6(AsO_4)_4$,[10] $Ca(NH_4)AsO_4$. $7H_2O$,[11] $Ca(NH_4)AsO_4.6H_2O$,[6] and $Ca_3(NH_4)H_2(AsO_4)_3.3H_2O$.[2] Lefèvre also isolated a calcium sodium pyroarsenate, $Ca_4Na_1(As_2O_7)_3$.

Calcium Thioarsenites.—By the action of concentrated calcium hydrosulphide solution on arsenic trisulphide under varying conditions several different compounds can be obtained. The following formulæ have been given for these : $CaS.As_2S_3.11H_2O$, $CaS.4As_2S_3.10H_2O$, $CaS.9As_2S_3.10H_2O$, and $7CaS.As_2S_3.25H_2O$.[12]

Calcium Thio-oxyarsenate, $Ca_3(AsOS_3)_2.20H_2O$, is obtained as colourless needles by the action of the corresponding sodium salt on a solution of calcium chloride in alcohol.[13] It is unstable.

[1] See p. 93; Debray, *Ann. Chim. Phys.*, 1861, [3], **61**, 419; Ditto, *ibid.*, 1886, [6], 8, 502; Lefèvre, *ibid*, 1892, [6], **27**, 5 ; Lechartier, *Compt. rend*, 1867, **65**, 172.
[2] de Schulten, *Bull. Soc. franç. Min.*, 1903, **26**, 18.
[3] Salkowski, *Jahresber.*, 1868, 231 ; Kotschoubey, *loc. cit.* ; Dufet, *Compt. rend.*, 1888, **106**, 1238 ; des Cloiseaux, *ibid.*, 1888, **106**, 1215.
[4] Dufet, *loc. cit.*
[5] Debray, *loc. cit.*
[6] Kotschoubey, *loc. cit.*
[7] de Schulten, *loc. cit.* ; Smith, *loc. cit.*
[8] Robinson, *loc. cit.*
[9] Smith, *loc. cit.*
[10] Lefèvre, *Compt. rend.*, 1889, **108**, 1058 ; *Ann. Chim. Phys.*, 1892, [6], **27**, 5.
[11] Bloxam, *Chem. News*, 1886, **54**, 168, 193.
[12] Nilson, *J. prakt. Chem.*, 1876, [2], **14**, 1 ; Kruss, *Annalen*, 1884, **225**, 35.
[13] McCay and Foster, *Zeitsch. anorg. Chem.*, 1904, **41**, 452.

CALCIUM AND ANTIMONY.

Calcium Antimonide, Ca_3Sb_2.—When antimony and calcium are heated together they combine so energetically that the resulting anti-monide is fused by the heat of the reaction.[1] Lebeau prepared it in the electric furnace. On treating with water it gives no antimony hydride, because the heat of reaction is so great as to raise the temperature of the products above the decomposition temperature of the hydride. By reducing calcium chloride with an alloy of sodium and antimony a product is obtained containing 7·6 per cent. of calcium, and giving, on treatment with water, hydrogen containing a large amount of antimony.[2]

Calcium Pyrothioantimonite, $Ca_2Sb_2S_3.15H_2O$, is obtained by dissolving antimony sulphide in calcium hydrosulphide. On evaporating *in vacuo* beautiful, colourless, triclinic crystals separate. These are soluble in water without decomposition.[3] By concentrating the hot solution a red crystalline compound, $SbS_2.CaOH$, is formed.

Calcium Antimonate, $CaSb_2O_6.6H_2O$, is obtained as a white amorphous precipitate by the action of an alkali antimonate on calcium chloride solution,[4] or of antimonic acid on calcium acetate.[5]

A yellow, noncrystalline calcium thioantimonate of uncertain formula has been described,[6] and also a chlorantimonate, $Ca(SbCl_6)_2.9H_2O$, crystallising in very long hygroscopic needles.[7]

CALCIUM AND VANADIUM.

Calcium Orthovanadate, $Ca_3(VO_4)_2$, is obtained by the decomposition of the sodium salt with calcium chloride. It is decomposed by the action of water into calcium pyrovanadate and calcium hydroxide.[8]

Compounds of tricalcium orthovanadate with calcium haloids, similar to the phosphate and arsenate halogen compounds, have also been described.[9]

Calcium Pyrovanadate, $Ca_2V_2O_7$.—Two hydrates have been described, $Ca_2V_2O_7.2·5H_2O$, obtained as a white amorphous powder by precipitating calcium chloride with sodium pyrovanadate and drying at 100° C.,[10] and $Ca_2V_2O_7.2H_2O$, obtained as colourless needles by precipitating an excess of calcium chloride with ammonium vanadate in ammoniacal solution.[11] The water of crystallisation is easily driven off by heat, leaving a yellow powder. The salt is readily soluble in dilute acids.

Calcium Metavanadate, $Ca(VO_3)_2$.—A tetrahydrate, $Ca(VO_3)_2.4H_2O$, separates as yellowish-white crystals on evaporating a mixture of an alkali vanadate and calcium chloride solutions.[12] It loses all its water at 180° C. On treating a mixture of ammonium metavanadate

[1] Moissan, *Compt. rend.*, 1898, **127**, 584; *Ann. Chim. Phys.*, 1899, [7], **18**, 289.
[2] Caron, *Compt. rend.*, 1859, **48**, 440.
[3] Pouget, *ibid.*, 1898, **126**, 1792.
[4] Heffter, *Pogg. Annalen*, 1852, **86**, 418.
[5] Senderens, *Bull. Soc. chim.*, 1899, [3], **21**, 56.
[6] Rammelsberg, *Pogg. Annalen*, 1841, **52**, 215.
[7] Weinland and Feige, *Ber.*, 1903, **36**, 244.
[8] Manasse, *Annalen*, 1887, **240**, 23.
[9] Hautefeuille, *Compt. rend.*, 1873, **77**, 896; Ditte, *ibid.*, 1883, **96**, 846, 1226; *Ann. Chim. Phys.*, 1886, [6], **8**, 502; see also Ephraim, *Zeitsch. anorg. Chem.*, 1903, **35**, 71.
[10] Roscoe, *J. Chem. Soc.*, 1871, **24**, 23.
[11] Ditte, *Compt. rend.*, 1887, **104**, 1705.
[12] Berzelius, *Pogg. Annalen*, 1831, **22**, 57; Norblad, *Ber.*, 1875, **8**, 126; Manasse, *loc. cit.*

and calcium chloride solutions with alcohol, bright yellow needles of the trihydrate, $Ca(VO_3)_2.3H_2O$, are obtained.[1]

Double Salts.—A double acid calcium potassium vanadate is known, $CaO.4K_2O.10V_2O_5.22H_2O$.[2]

Acid Salts.—A number of acid salts have been obtained by precipitation from acid solutions; among them are, $CaO.2V_2O_5.9H_2O$,[3] $CaO.2V_2O_5.6H_2O$, $3CaO.4V_2O_5.15H_2O$, $3CaO.8V_2O_5.26H_2O$,[4] and $CaO.3V_2O_5.12H_2O$.[5] They all form red crystals.

Calcium Pervanadate, CaV_2O_8, is obtained as a yellow microcrystalline precipitate by treating a solution of ammonium vanadate and calcium chloride with acidified hydrogen peroxide and alcohol.[1]

CALCIUM AND COLUMBIUM.

Calcium Pyro- and Meta-columbates (niobates).—A calcium columbate is present in the mineral *pyrochlore*. If columbic acid, potassium chloride, and a large excess of calcium fluoride are fused together at bright red heat for several hours, calcium pyrocolumbate, $Ca_2Cb_2O_7$, is obtained in orthorhombic prisms. If the potassium chloride is in excess, the metacolumbate, $Ca(CbO_3)_2$, is formed in long, thin needles.[6] The pyrocolumbate may also be obtained by precipitating a solution of calcium chloride with potassium columbate, fusing the precipitate with anhydrous calcium chloride, and lixiviating with water, whilst the metacolumbate is prepared by fusing the precipitated salt with boric acid and lixiviating with dilute hydrochloric acid.[7] The density of the latter is 4·12.

CALCIUM AND TANTALUM.

Calcium Pyro- and Meta-tantalate, $Ca_2Ta_2O_7$ and $Ca(TaO_3)_2$ respectively, have been obtained by Joly by methods similar to those which he employed for the preparation of the columbates.[6]

Calcium Potassium Pertantalate, $CaKTa_2O_8.4.5H_2O$, is precipitated as a crystalline powder by the action of potassium pertantalate on calcium chloride solution. It forms rhombic prisms insoluble in cold water. It is decomposed by warming with water, the acid separates and the solution becomes alkaline.[8]

CALCIUM AND CARBON.

Calcium Carbide, CaC_2.—Wöhler observed that a substance which evolved acetylene on treatment with water, apparently calcium carbide, was obtained by the action of carbon on a zinc-calcium alloy.[9] Calcium carbide may also be formed by the action of amorphous carbon on metallic calcium, calcium hydride, or calcium nitride,[10] by heating the compound

[1] Scheuer, *Zeitsch. anorg. Chem.*, 1898, 16, 284.
[2] Manasse, *loc. cit.*
[3] von Hauer, *J. prakt. Chem.*, 1860, [1], 80, 324.
[4] Manasse, *loc. cit.*; Berzelius, *loc. cit.*
[5] Ditte, *Compt. rend.*, 1887, 104, 1705.
[6] Joly, *ibid.*, 1875, 81, 267.
[7] Larsson, *Zeitsch. anorg. Chem.*, 1896, 12, 188.
[8] Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.*, 1899, 20, 344.
[9] Wöhler, *Annalen*, 1862, 124, 220.
[10] Moissan, *Compt. rend.*, 1898, 127, 917.

$CaC_2.C_2H_2.4NH_3$, produced by the absorption of acetylene by calcium ammonium,[1] and by a secondary reaction when calcium chloride or a mixture of calcium chloride and calcium fluoride is electrolysed with carbon electrodes.[2] It was the work of Moissan in Paris,[3] and independently of Willson at Spray in North Carolina, U.S.A.,[4] that made possible the production of calcium carbide on a commercial scale by fusing together lime and carbon in the electric furnace.

The physical and chemical properties were first studied by Moissan. The pure compound forms transparent, colourless crystals, of density 2·22 at 18° C.,[5] but the commercial product is coloured by iron and other impurities. The crystalline structure is complex, but probably orthorhombic.[6] The melting-point is above the temperature of fusion of platinum.

It was formerly stated that calcium carbide is produced from its elements with the absorption of heat,[7] but, according to later investigations, it has a positive heat of formation of 13·15 Cal.[8] As might be expected, therefore, it dissociates at a very high temperature, above 1475° C.,[9] calcium volatilising and leaving the carbon behind.[10,11] The action is accelerated by certain salts, especially calcium fluoride.

Calcium carbide is insoluble in all known solvents. It is not reduced by hydrogen, but it reacts with the halogens between 250° and 300° C. with incandescence,[12] burns in oxygen at red heat forming carbonate, and in sulphur at 500° C. forming calcium sulphide and carbon disulphide. With water and with dilute acids it produces acetylene. It reacts with gaseous hydrochloric acid at red heat, becomes incandescent when treated with oxidising agents, and reduces oxides and salts, forming lime and the free element or carbide.[13] It also reduces a number of organic compounds to carbon.[14]

[1] Moissan, Compt. rend., 1898, 127, 911, but see Hackspill and Bofolfsen, ibid., 1921, 173, 151; Botolfsen, Ann Chim., 1922, [9], 18, 1. Botolfsen stated that the pure compound can only be obtained by direct union of calcium and carbon in an atmosphere of argon at about 925°–975° C

[2] Moissan, Compt. rend., 1904, 138, 661, 1194; Bulher, ibid., 904.

[3] Moissan, ibid., 1892, 115, 1031; 1894, 118, 501.

[4] Willson, English Patents, 16705 (1894); 15360 (1895).

[5] But see Botoltsen, loc. cit.

[6] Warren, Amer. J. Sci., 1921, [5], 2, 120.

[7] de Forcrand, Compt. rend., 1895, 120, 682.

[8] Moissan, ibid., 1904, 138, 243; Guntz and Bassett, ibid., 1905, 140, 863.

[9] de Kay Thompson, Met. Chem. Eng., 1910, 8, 279, 324. This seems to be a rather low temperature in view of the temperatures reached in manufacture.

[10] Moissan, Compt. rend., 1898, 126, 302; Gin and Leleux, ibid., 1898, 126, 236; Briner and Kuhne, ibid., 1913, 156, 620; Botoltsen, loc. cit., Erlwein, Warth, and Beutner, Zeitsch. Elektrochem., 1911, 17, 177. These investigators thought that a subcarbide might be formed.

[11] According to Ruff and Foerster, Zeitsch. anorg. Chem., 1923, 131, 321, the dissociation pressure of calcium carbide is 1 mm. at 1825°±50° C. and 1 atmosphere at 2500°± 50° C., the vapour being mainly calcium, not more than 4·5 per cent. being carbide vapour at 1 atmosphere.

[12] See also Barnes, Chem. News, 1919, 119, 260.

[13] Venable and Clarke, J. Amer. Chem. Soc., 1895, 17, 306; Moissan, Compt. rend., 1897, 125, 839; Warren, Chem. News, 1897, 75, 2; Bamberger, Ber., 1898, 31, 451; Tarugi, Gazzetta, 1899, 29, i, 509; Frohlich, Zeitsch. angew. Chem., 1899, 12, 1177; Geelmuyden, Compt. rend., 1900, 130, 1026; Neumann, Chem. Zeit., 1900, 24, 1013; 1902, 26, 716, 1108; Zeitsch Elektrochem., 1902, 8, 772, 939; von Kugelgen, Chem. Zeit., 1900, 24, 1060; Zeitsch. Elektrochem., 1900–1901, 7, 541, 557, 573; 1902, 8, 781; Pring, Trans. Chem. Soc., 1905, 87, 1530.

[14] Sandmann, Zeitsch. angew. Chem., 1902, 15, 543.

At high temperatures calcium carbide absorbs nitrogen, forming calcium cyanamide, $CaCN_2$,[1] and at 100° C. it absorbs acetylene, giving the compound $CaC_2.C_2H_2$.[2]

The reaction by which carbide is produced is reversible.[3]

$$CaO + 3C \rightleftharpoons CaC_2 + CO.$$
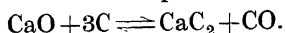
The heat absorbed in the reaction from left to right at ordinary temperatures is 111 Cal., with a negative temperature coefficient of 0·0033 Cal. per degree.[4] Under the conditions of manufacture the pressure of carbon monoxide cannot be less than $\frac{1}{3}$ atmosphere, which will be the amount formed by the action of atmospheric oxygen on the carbon. The temperature at which this pressure is reached is 1655°–1720° C., calculated from the heat of reaction and from the pressure determinations at lower temperatures, by means of the equation $4\cdot57 \log_{10} p_2/p_1 = Q(1/T_1 - 1/T_2)$ where Q is the quantity of heat absorbed, and p_1 and p_2 the pressures at the absolute temperatures T_1 and T_2.[5] This could not be verified experimentally, because, under the conditions of the experiment, the calcium carbide breaks up into its elements a little above 1475° C., but in practice this temperature must evidently be exceeded before carbide can be formed. If the carbide is cooled in an atmosphere of carbon monoxide there is a back reaction in the neighbourhood of the solidifying point, but the effect is limited to the surface in contact with the gas, and so is not important on the large scale.[6]

On heating the carbide with carbon in the electric furnace the carbon is dissolved.[7]

The manufacture of calcium carbide consists simply in the fusion of a mixture of lime and carbon at the high temperature of the electric furnace. Carbon or graphite electrodes are used. The furnaces in use may be divided into two classes—intermittent and continuous. Although the intermittent process, by which the carbide is gradually built up into a huge block during the operation of the furnace, produces the best quality of carbide, it is falling into disfavour because it is uneconomical to work. The furnace has to be allowed to cool, and is then dismantled in order to remove the carbide and to recharge.

The continuous furnace is made of sheet iron lined with carbon and mounted on wheels. It is open at the top for the admission of the charge. One electrode consists of several blocks of carbon hanging over the top of the furnace, the other forms the hearth or bottom of the furnace. An outlet near the base allows the molten carbide to be drawn off from time to time, whilst fresh charge is fed in at the top. The carbide is run into cast-iron trays and allowed to cool. To increase the fusibility

[1] Erlwein, *Zeitsch. angew. Chem.*, 1903, 16, 533 ; Frank, *ibid.*, 536, 659 ; Rothe, *ibid.*, 658. See later.

[2] Moissan, *Compt. rend.*, 1903, 136, 1522.

[3] Rothmund, *Zeitsch. anorg. Chem.*, 1902, 31, 136 ; Frank, *Zeitsch. angew. Chem.*, 1905, 18, 1734.

[4] de Kay Thompson, *Trans. Amer. Electrochem. Soc.*, 1909, 16, 197. This author found 121 Cal., but the value in the text is obtained by recalculation from more recently determined values for the heat of formation of calcium oxide and carbide.

[5] de Kay Thompson, *Met. Chem. Eng*, 1910, 8, 279, 324. Employing his figure for the heat of reaction, Thompson found the minimum temperature to be 1800°–1875° C. See also Rothmund, *Zeitsch. anorg. Chem.*, 1902, 31, 136 ; Rudolfi, *ibid.*, 1907, 54, 170.

[6] Hutton and Petavel, *Proc. Roy Soc.*, 1907, 79A, 155.

[7] Kahn, *Compt. rend.*, 1906, 143, 49.

of the product an excess of lime is used, so that there is a smaller volume of acetylene per unit weight than in the case of block carbide. There is also a gradual accumulation of slag and impurities which cling to the sides of the furnace and fill it up.

The Alby furnace, used at Odda in Norway, which is of this type, can produce 7–8 tons of carbide per day and takes a current of 28,000 ampères at 50 volts. The temperature is between 2000° and 3000° C.[1] At Niagara the Horry furnace is in use. It is in the form of a large revolving wheel by which the charge, as the operation is completed, is gradually carried past the fixed electrodes.

The lime and carbon are introduced in the form of lumps, 5–8 cm. in diameter, so the lime must be such as to calcine without falling into powder. The natural impurities should not exceed more than 4–5 per cent. of the burnt lime, and of this not more than 2 per cent. should consist of magnesium and aluminium oxides which make the carbide less friable. The formation of iron silicide should be avoided, as it injures the furnace and crushing apparatus and may be the cause of explosions. If the carbide is to be used for the production of acetylene, phosphorus is dangerous and sulphur disagreeable but not dangerous.[2] The carbon may be in the form of anthracite, coke, retort carbon, or wood charcoal, but the ash content must be very low and the phosphorus absent.

As water power is desirable for the electric current requirements, production on the largest scale is in Scandinavia and America. There was, at first, over-production of carbide, owing to a too great optimism as to the value of acetylene as an illuminant, and many factories had to be closed again and still remain closed (1922).[3] The carbide first produced contained too many impurities. Now, however, a better product is obtained, and there is an increasing demand due to the use of acetylene in oxyacetylene welding, and flares in marine work. More important still has been the use of carbide as a starting-point in the manufacture of cyanamide and other synthetic nitrogen products.[4]

Other uses for it have also been proposed ; for example, the formation of metallic alloys from oxides or chlorides, the carbide being used as a de-oxidising flux with borax, sodium chloride, or calcium chloride,[5] and the preparation of argon from the atmosphere by circulating air over a mixture of calcium carbide and chloride at 800° C. to absorb oxygen and nitrogen.[6] The production of alcohol from carbide has apparently been tried successfully on a small scale in Switzerland.[7] Its application as an explosive in mining operations by using carbide cartridges containing an air-space, so as to give an explosive mixture of air and acetylene, has also been suggested.[8]

Instead of using water in the liquid form for the production of

[1] See Tucker, Alexander, and Hudson, *Trans. Amer. Electrochem. Soc.*, 1909, **15**, 411.

[2] Witherspon, *J. Soc. Chem. Ind.*, 1913, **32**, 113.

[3] See *Chem. Met. Eng.*, 1922, **27**, 832.

[4] See Calcium Cyanamide, p. 117

[5] Hodgkinson, *J. Soc. Chem. Ind.*, 1914, **33**, 445 ; see also Neumann, *Zeitsch. Elektrochem.*, 1902, 8, 772.

[6] Fischer, *Ber.*, 1907, **40**, 1110.

[7] Tait and Fletcher, *App. Chem. Reports*, 1920, **5**, 448 ; Hennig, *Chem. Abs.*, 1920, **14**, 2675 ; see also Monier-Williams, *Power Alcohol* (Henry Frowde and Hodder & Stoughton), 1922, p. 194.

[8] Guédras, *Compt. rend.*, 1904, **139**, 1225.

acetylene, the carbide may be heated with salts containing water of crystallisation.[1]

Calcium Formate, $Ca(HCO_2)_2$, forms anhydrous rhombic crystals of density 2·015 when calcium hydroxide or carbonate is neutralised by formic acid.[2] It can also be obtained by the action of carbon monoxide and steam on calcium hydroxide at 250°–300° C. At higher temperatures, 500°–600° C., calcium formate in the presence of water produces calcium carbonate and hydrogen.[3] It is only slightly soluble in alcohol, but 100 grm. of water dissolve 16·6 grm. of the salt at 20° C.[4] The solubility increases slightly with temperature. The degree and nature of the electrolytic dissociation of calcium formate in solution have been studied.[5]

Calcium Acetate, $Ca(C_2H_3O_2)_2$, crystallises from hot solutions in thin needles with 1 molecule, from cold solutions with 2 molecules of water of crystallisation. The transition point is at 84° C.[6] At 20° C. 100 grm. of water dissolve 34·73 grm. of anhydrous calcium acetate, and at 100° C. 29·65 grm.[6] The electrolytic dissociation of the salt in solution, calculated from the freezing-point lowering,[7] is much greater than that indicated by the electrical conductivity.[8] The densities of solutions of calcium acetate have been determined.[9]

Acetone is prepared commercially by the distillation of calcium acetate. The reaction is practically quantitative, but losses occur due to the further decomposition of the acetone vapours coming into contact with the heated walls of the containers.[10]

With acetic acid and calcium nitrate a crystallised double compound is formed, and an acid salt, $Ca(C_2H_3O_2)_2.C_2H_3O_2$, is obtained by treating solid calcium hydroxide with concentrated acetic acid.[11]

Calcium Oxalate, CaC_2O_4, crystallises from very dilute solutions in the cold with 3 molecules of water, and at room temperature with 1 in monoclinic crystals, its density being 2·2.[12] The water of crystallisation is only completely removed at 200° C., and at red heat the salt is decomposed into calcium carbonate and carbon monoxide. Calcium oxalate is only slightly soluble in water.[13] By electrical conductivity methods, Kohlrausch found a solubility of 5·6 grm. per litre of the

[1] Atkins, *Engineering*, 1906, **81**, 261 ; Turner, *Amer. Chem. J.*, 1907, **37**, 106 ; Masson, *Trans. Chem. Soc.*, 1910, **97**, 851. For further details on the manufacture of calcium carbide see Pring, *The Electric Furnace* (Longmans, Green & Co.), 1921, pp. 11, 102, 435 ; Martin, *Industrial Chemistry, Inorganic* (Crosby Lockwood & Son), 1917, vol. ii, p. 409 ; Thorpe, *Dict. Appl. Chem.* (Longmans, Green & Co.), 1921, vol i, p. 738 ; Moissan, *Traité de Chimie Minérale* (Masson et Cie), 1904, vol. iii, p. 690 ; Blount, *Practical Electrochemistry* (Archibald Constable & Co., Ltd.), 1906, p. 208 ; Borchers, *Electric Furnaces*, translated by Solomon (Longmans, Green & Co), 1908, p. 104 ; Rideal, *Industrial Electrometallurgy* (Baillière, Tindall & Cox), 1918, p. 173.

[2] Heusser, *Jahresber.*, 1851, 434 ; Schröder, *Ber.*, 1881, **14**, 21.

[3] Levi and Piva, *Annali Chim. appl.*, 1916, **5**, 271.

[4] Stanley, *Chem. News*, 1904, **89**, 193 ; Lumsden, *Trans. Chem. Soc.*, 1902, **81**, 350.

[5] Calame, *Zeitsch. physikal. Chem.*, 1898, **27**, 401 ; Schlesinger and Bunting, *J. Amer. Chem. Soc.*, 1919, **41**, 1934, solutions in anhydrous formic acid.

[6] Lumsden, *loc. cit.*

[7] Calame, *loc. cit.*

[8] MacGregory, *Wied. Annalen*, 1896, **51**, 126.

[9] Franz, *J. prakt. Chem.*, 1872, [2], **5**, 298 ; see Gerlach, *Zeitsch. anal. Chem.*, 1888, **27**, 289.

[10] Goodwin and Sterne, *J. Ind. Eng. Chem.*, 1920, **12**, 240.

[11] Colson, *Compt. rend.*, 1903, **137**, 1061 ; see also Villiers, *ibid.*, 1877, **84**, 774.

[12] Schröder, *Ber.*, 1879, **12**, 564.

[13] See Estimation of Calcium, p. 146 *et seq.*

anhydrous salt at 18° C.,[1] but much higher values have been given.[2] It is practically insoluble in a dilute solution of ammonium oxalate,[3] but some salts, for example magnesium and zinc chlorides, increase the solubility.

Double salts are formed with calcium chloride, for example, $CaC_2O_4.CaCl_2.7H_2O$ and $3CaC_2O_4.CaCl_2.8H_2O$.[4]

Calcium oxalate is found in many plants. In rhubarb, for instance, it occurs in aggregates of needle-like crystals. It is found in considerable quantity in certain lichens growing on limestone.

Calcium Carbonate, $CaCO_3$.—Calcium carbonate is one of the most frequently occurring compounds of calcium in both inorganic and organic nature. It is often found in large masses almost chemically pure. *Chalk, limestone, marble, calcspar*, coral, and the shells of molluscs are the principal sources. It is also found as *dolomite*, in which some of the calcium is replaced by magnesium, and as the double calcium lead carbonate, *plumbocalcite*.

Two crystalline forms undoubtedly exist. The most widely distributed is the hexagonal form, *calcite, calcspar*, or *Iceland spar*, showing marked double refraction. *Aragonite* in rhombic crystals is much rarer. Other forms have been described—conchite,[5] ktypeite, or vaterite,[6] and lublinite.[7] According to more recent investigations, however, these latter are identical with one or other of the two well-known forms and a third form, μ-calcium carbonate, consisting of microscopic hexagonal plates of density 2·54, which is obtained by precipitation at 60° C., but is always contaminated with the other two.[8] Another form, α-calcium carbonate, only stable at very high temperatures and with optical properties apparently identical with those of calcite, has also been mentioned.[9] The apparently amorphous varieties probably consist of minute crystals of calcite.

Marble and limestone consist of small interlocking calcite crystals.

Calcite and aragonite form one of the earliest recognised cases of polymorphism. Both are anhydrous calcium carbonate, but, besides the difference in crystalline form already noted, there is a difference in density, which is 2·715 for calcite and 2·934 for aragonite. Calcite is isomorphous with sodium nitrate, and aragonite with strontianite. There is an extensive literature of the mutual relations of calcite and aragonite, the former being the stable variety under ordinary conditions. When calcium carbonate is formed by precipitation, it is very probable that, in accordance with Ostwald's rule, one of the unstable forms, μ-calcium carbonate or aragonite, is first obtained, and that this changes with more or less rapidity into calcite. In some cases, owing to the high temperature or to the catalysing effect of the salts present, the velocity

[1] Kohlrausch. *Zeitsch. physikal. Chem.*, 1908, **64**, 129; see also Richards, McCaffrey, and Bisbee, *Zeitsch. anorg. Chem.*, 1901, **28**, 71.

[2] Herz and Muhs, *Ber.*, 1903, **36**, 3715.

[3] Richards, McCaffrey, and Bisbee, *loc. cit.*

[4] Fritzsche, *Jahresber.*, 1864, 372.

[5] Kelly, *J. Chem. Soc.*, 1901, **80**, Abs. ii, 168.

[6] Vater, *Zeitsch. Kryst. Min.*, 1893, **21**, 433; 1897, **27**, 477; 1902, **35**, 149; Lacroix, *Compt. rend.*, 1898, **126**, 602; Meigen, *Chem. Zeit.*, 1910, **34**, 1015.

[7] Morozewicz, *Zeitsch. Kryst. Min.*, 1911, **48**, 522.

[8] Johnston, Merwin, and Williamson, *Amer. J. Sci.*, 1916, [4], **41**, 473.

[9] Boeke, *Jahrb. Miner.*, 1912, i, 91, see *J. Chem. Soc.*, 1912, **102**, Abs. ii, 760.

of transformation may be so great that calcite appears to be the first precipitated.[1]

In the dry state aragonite is not changed into calcite with appreciable rapidity until a temperature above 400° C. is reached. At 470° C. the change takes place in a few minutes.[2] If under any conditions aragonite can be the stable form, it must be at very low temperatures. The transition temperature has been given as $-43° \pm 5°$ C., rising 1° C. per 40 atmospheres increase of pressure.[3] It can only be in the coldest regions of the earth, therefore, that natural aragonite is the stable form. The following are probably the main conditions under which aragonite forms in nature : (a) through organic agencies, for example shells ; (b) by deposition from hot springs ; (c) when an isomorphous carbonate is present to serve as a nucleus ; (d) by chemical precipitation in certain saline waters in the presence of sulphate. The preservation of aragonite in any but recent geological formations may depend on its having been kept dry, or on the presence of impurities, which are more frequent in aragonite than in calcite and which reduce the rate of transformation by water by reducing the solubility below that of calcite. In older rocks, fossil shells of such a type that they were presumably aragonite originally, now consist of calcite.[4] The change from aragonite to calcite is accompanied by a 10 per cent. increase in volume. The heat of transformation is so small, however, that there appears to be some doubt as to whether it is positive or negative.[5] It is possible that it may be positive at ordinary temperatures and negative at higher ones.[6]

μ-Calcium carbonate is too unstable to be found as a mineral, and a-calcium carbonate is only stable above 970° C., the temperature of transition from calcite.[7]

A number of colour tests have been suggested for distinguishing aragonite from calcite in minerals. These depend on the different reactivities of the two modifications towards different salt solutions.[8]

Calcium carbonate may be prepared by precipitation of a soluble calcium salt with an alkali carbonate, or by neutralisation of calcium

[1] Rose, J. prakt. Chem., 1861, [1], 82, 351 ; Pogg. Annalen, 1837, 42, 353 ; 1861, 112, 43 ; Jahresber., 1856, 878 ; 1858, 126 , Vater, Zeitsch. Kryst. Min , 1893, 21, 433 ; 1895, 24, 366, 378 ; 1898, 30, 295 , 1899, 31, 538 ; Adler, Zeitsch. angew. Chem., 1897, 10, 431 ; Stocks, J. Soc. Chem. Ind., 1902, 21, 527 ; Foote, Zeitsch. physikal. Chem., 1900, 33, 740 ; Meigen, Jahrb. Miner., 1903, ii, 19 ; Chem. Zentr., 1903, ii, 1411 ; 1905, i, 1363 ; Hatschek, Chem. Zeit., 1909, 33, 49 ; Leitmeier, Jahrb. Miner , 1910, i, 49 ; Vetter, Zeitsch. Kryst. Min., 1911, 48, 45.

[2] Laschtschenko, J. Russ. Phys. Chem. Soc., 1911, 43, 793 ; Sosman, Hostetter, and Merwin, J. Wash. Acad Sci., 1915, 5, 563 ; Johnston, Merwin, and Williamson, loc. cit. See also Rose, Pogg. Annalen, 1860, 111, 156 ; Miron and Bruneau, Compt. rend., 1881, 95, 182 ; Bourgeois, Ann. Chim. Phys., 1883, [5], 29, 486 ; Bull. Soc. chim., 1887, [2], 47, 81 ; Adler, loc. cit. ; Vater, loc. cit. ; Foote, loc. cit.

[3] Bäckström, Zeitsch. physikal. Chem , 1921, 97, 179 ; see also Johnston, Merwin, and Williamson, loc. cit.

[4] Johnston, Merwin, and Williamson, loc. cit. ; see also Johnston and Williamson, J. Geol., 1916, 24, 729, see J. Chem. Soc., 1917, 112, Abs. ii, 213.

[5] Le Chatelier, Compt. rend., 1893, 116, 390 ; de Forcrand, ibid , 1908, 146, 511 ; Laschtschenko, loc. cit. ; Favre and Silbermann, Ann. Chim. Phys., 1853, [3], 37, 434 ; Backstrom, loc. cit., found − 0·67 Cal.

[6] Johnston, Merwin, and Williamson, loc. cit.

[7] Boeke, loc. cit.

[8] Meigen, J. Chem. Soc., 1901, 80, Abs. ii, 692 ; Chem. Zeit., 1910, 34, 1015 ; Hutchinson, J. Chem. Soc., 1903, 84, Abs. ii, 379 ; Thugutt, Chem. Zentr., 1910, ii, 1084 ; Niederstadt, Zeitsch angew. Chem., 1912, 25, 1219 ; Quercigh, Atti R. Accad. Lincei, 1915, [5], 24, i, 1231.

hydroxide solution with carbon dioxide. The latter is not an instantaneous process but may take a considerable time before it is complete. It is probably governed by the rate of hydration of carbon dioxide.[1]

By fusion of the precipitated carbonate with a mixture of sodium and potassium chlorides, calcite in a visibly crystalline form may be obtained.[2]

The specific heat of calcium carbonate at ordinary temperatures is 0·2027.[3] Regnault gave the following values for the specific heats of the different mineral forms at 99° C.[4] :—

Iceland spar	.	.	.	0·20858
Aragonite	.	.	.	0·20850
White marble	.	.	.	0·21585
Grey marble	.	.	.	0·20989
White chalk	.	.	.	0·21485

Calcite is phosphorescent under the cathode rays,[5] and some specimens also when heated,[6] or on insolation.[7]

On heating calcium carbonate it decomposes into calcium oxide and carbon dioxide.[8] The reaction is reversible at high temperatures, and for every temperature there is a corresponding equilibrium pressure of carbon dioxide.[9] This behaviour is to be expected if the system consists of two solid phases, calcium oxide and calcium carbonate, and a vapour phase, carbon dioxide. At low temperatures dissociation and re-absorption proceed very slowly, and depend very much on the condition of the solid phases. Jolibois and Bouvier found that the reaction is not completely reversible when pure calcium carbonate alone forms the starting-point. A mixture of calcium oxide and calcium carbonate must be used.[10] Probably the difficulty is of purely mechanical origin. These authors regarded it as an indication that a solid solution of calcium oxide in calcium carbonate is formed.[11]

The following values have been given for the dissociation pressures of calcium carbonate at different temperatures[12] :—

Temperature, °C	500	550	600	650	700	750	800	850	900	950	1000
Pressure, mm. mercury	0·11	0·57	2·35	8·20	25·3	68	168	373	773	1490	2710

The temperature of dissociation at atmospheric pressure, 760 mm., according to Riesenfeld is 908 +5° C. Hedvall found 913°–923° C.,[13]

[1] Vorländer and Strube, *Ber.*, 1913, **46**, 172; Theil, *ibid.*, 1913, **46**, 241, 867.

[2] Bourgeois, *Ann. Chim. Phys.*, 1883, [5], **29**, 486.

[3] Nernst, Koref, and Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 247.

[4] Regnault, *Ann. Chim. Phys.*, 1841, [3], **1**, 129. Kopp found 0·206 for calcspar and 0·203 for aragonite, *Annalen*, *Suppl.*, 1864-5, **3**, 295.

[5] Crookes, *Proc. Roy. Soc.*, 1881, **32**, 206; de Boisbaudran, *Compt. rend.*, 1886, **103**, 468.

[6] Pisani, *Compt. rend.*, 1914, **158**, 1121.

[7] Headden, *Amer. J. Sci.*, 1906, [4], **21**, 301.

[8] See Calcium Oxide, p. 50.

[9] Debray, *Compt. rend.*, 1867, **64**, 603; Lemoine, *Ann. Chim. Phys.*, 1872, [4], **27**, 308.

[10] Jolibois and Bouvier, *Compt. rend.*, 1921, **172**, 1182.

[11] See also Zavrieff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, i, 34.

[12] Riesenfeld, *J. Chim. phys.*, 1909, **7**, 561; see also Zavrieff, *Compt. rend.*, 1907, **145**, 428; higher values were obtained by Le Chatelier, *Compt. rend.*, 1886, **102**, 1243.

[13] Hedvall, *Zeitsch. anorg. Chem.*, 1916, **98**, 47.

and Johnston 898° C.[1] The latter obtained the following equation for the pressure-temperature curve :—

$$\log_{10}p = -9340/T + 1\cdot1 \log_{10}T - 0\cdot0012T + 8\cdot882,$$

where p is the pressure in mm. mercury and T the absolute temperature.

Since aragonite is the unstable form, it should have a higher dissociation pressure than calcite, but at the temperature at which rapid transformation into calcite begins, the pressures are only of the order of $0\cdot01$ mm. and differences cannot be determined with accuracy.[2]

The molecular heat of formation of precipitated calcium carbonate from calcium oxide and carbon dioxide is $43\cdot3$ Cal., of calcspar $42\cdot0$ Cal., of aragonite $42\cdot6$ Cal., and of the carbonate at the temperature of decomposition under a pressure of 1 atmosphere $34\cdot76$ Cal.[3]

Marble is generally said to be of igneous origin, and Hall claimed to have obtained marble by the fusion of chalk,[4] but the experiments were repeated by later investigators without success.[5] Recently a substance of the characteristic appearance of marble has been obtained by heating anhydrous calcium chloride with hydrated sodium carbonate, or hydrated chloride with anhydrous carbonate, for eight hours at 300°–305° C. under 24 atmospheres pressure ; or by saturating with carbon dioxide, at room temperature, a paste of precipitated chalk with saturated sodium chloride solution, and heating for eight hours at 300°–305° C. under a pressure of 27 atmospheres.[6] Le Chatelier supposed that he had obtained evidence of fusion of calcium carbonate, with or without pressure, at 1020° C.,[7] but this was questioned by Joannis,[8] and also by Boeke,[9] who found that it partially dissociated but did not melt even when heated to 1400°–1500° C., under a pressure of carbon dioxide of 30 atmospheres, although the original fine powder became crystalline. In later experiments, however, the latter succeeded in fusing Iceland spar at 1289° C. in carbon dioxide at 110 atmospheres pressure,[10] but the work of Smith and Adams seems to indicate that the melting-point of calcium carbonate lies a little above 1340° C. under a pressure of about 1050 atmospheres.[11] An eutectic mixture containing 50 per cent. of calcium oxide fuses at 1240° ±1° C. under about 40 atmospheres pressure.[11]

Calcium carbonate is only very slightly soluble in water, but the solubility is greatly influenced by the concentration of carbon dioxide in solution,[12] and this in its turn depends on the concentration or partial pressure of the gas in the vapour space above the solution. This influence is explained by the hydrolysis of calcium carbonate by water, forming the more soluble calcium hydroxide when the partial pressure of carbon dioxide is low, and by the formation of calcium bicarbonate, which is also more soluble than the carbonate, when the partial pressure of carbon dioxide is high. After prolonged boiling of a suspension of calcium carbonate, the substance passing into solution is practically all calcium

[1] Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 938.
[2] Sosman, Hostetter, and Merwin, *J. Wash. Acad. Sci.*, 1915, **5**, 563.
[3] de Forcrand, *Compt. rend.*, 1908, **146**, 511.
[4] Hall, *Trans. Roy. Soc. Edinburgh*, 1799, 5.
[5] Rose and Siemens, *Pogg. Annalen*, 1863, **118**, 565 ; Becher, *Jahresber.*, 1886, 2301.
[6] Copisarow, *Trans. Chem. Soc.*, 1923, **123**, 785.
[7] Le Chatelier, *Compt. rend.*, 1892, **115**, 817, 1009.
[8] Joannis, *ibid.*, 1892, **115**, 934, 1296.
[9] Boeke, *Zeitsch. anorg. Chem.*, 1906, **50**, 244.
[10] Boeke, *Jahrb. Miner.*, 1912, **1**, 91, see *J. Chem. Soc.*, 1912, **102**, Abs. ii, 760.
[11] Smyth and Adams, *J. Amer. Chem. Soc.*, 1923, **45**, 1167.
[12] Bineau, *Ann. Chim. Phys.*, 1857, [3], **51**, 290.

hydroxide.[1]   By passing a very rapid stream of carbon dioxide through saturated lime-water at 15° C., a concentration of 2 29 grm. of calcium carbonate may be reached, but this only persists for a short time.[2]
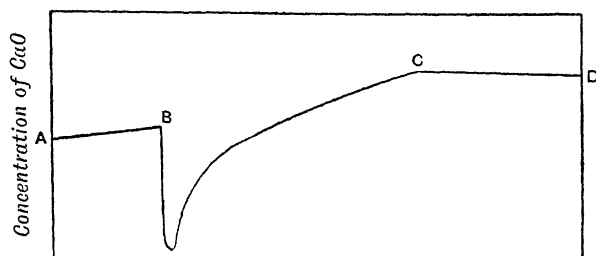
FIG. 5.

A study of the solubility of calcium carbonate is, therefore, a study of the equilibrium conditions in the ternary system, calcium oxide : carbon dioxide : water, and for any one temperature a pressure-concentration curve, consisting of three branches, might be drawn, as shown in Fig. 5, which gives a general, but not an accurate, indication of the course of the curve—the low-pressure part of the curve being on a much larger scale than the high-pressure part.

The branch AB represents the slightly increasing concentration of

Partial Pressure of CO_2 in Atmos.	Mgm. $CaCO_3$ per Litre, at 16° C.	Authority.
$3 16 \times 10^{-11}$	2000	
$2 80 \times 10^{-10}$	74	
$6 14 \times 10^{-8}$	18	Johnston and Williamson,
$3 73 \times 10^{-7}$	15·9	*J. Amer. Chem. Soc.*,
$3·85 \times 10^{-7}$	15 9	1916, **38**, 975.
$7·62 \times 10^{-6}$	22	
$2 15 \times 10^{-1}$	56	
$5 04 \cdot 10^{-4}$	74·6	
$3 33 \times 10^{-3}$	137·2	
$1·39 \times 10^{-2}$	223·1	
$5·01 \times 10^{-2}$	360·0	Schlösing, *Compt. rend.*,
$2 54 \times 10^{-1}$	663 4	1872, **74**, 1552 ; **75**, 70.
$5·53 \times 10^{-1}$	885·5	
$9·84 \times 10^{-1}$	1080	
1	1079	
2	1411	Engel, *Ann. Chim. Phys.*,
4	1820	1888, [6], **13**, 344.
6	2109	
15	2600 (at 25° C.)	McCoy and Smith, *J. Amer. Chem. Soc.*, 1911, **33**, 468.

[1] Cavazzi, *Gazzetta*, 1917, 47, ii, 49.   [2] Cavazzi, *ibid.*, 1916, 46, ii, 122.

the solution in contact with solid calcium hydroxide for partial pressures up to about 10^{-14} atmosphere, at which point, represented by B on the diagram, the solid phase, calcium carbonate, appears. The solubility then falls with increasing pressure to a minimum value at about $3\cdot8\times10^{-7}$ atmosphere, as calculated by Johnston and Williamson from the solubility product.[1] The solubility rises again, rapidly at first and then more gradually, until, at about 15 atmospheres pressure, marked by point C, a fresh solid phase, calcium bicarbonate, should appear.[2] The line CD shows a slightly decreasing concentration of bicarbonate with further increase of pressure.

It is probable that even at the minimum concentration of calcium ions in solution, which is the maximum of carbonate ions, more than 50 per cent. of the negative ions still consist of hydroxyl and bicarbonate ions.

The solubility of calcium carbonate under normal atmospheric conditions, at a partial pressure of carbon dioxide of 3×10^{-4} atmospheres, is 63 mgm. per litre. The failure of some investigators to state the partial pressures under which their experiments were conducted makes difficult any comparison between the determinations made. It is also possible that in some cases equilibrium was not reached.[3]

The solubility of calcium carbonate decreases with rise of temperature. The following values have been obtained for the solubility of calcite at different temperatures under a partial pressure of $3\cdot2\times10^{-4}$ atmospheres[4] :—

Temperature, ° C.	1	21	23	30
Mgm. $CaCO_3$ per litre	82	60	57	55

The solubility of aragonite is greater than that of calcite,[5] in accordance with the general relationship between stable and unstable forms. The ratio of solubilities has an average value of $1\cdot07$,[6] but there is a tendency for this to decrease as the temperature falls,[4] which suggests that aragonite becomes the stable form at low temperatures.[7]

A convenient method of expressing the solubility is by the solubility product constant, $[Ca^{\cdot\cdot}]\times[CO_3'']$, from which the saturation concentration for any given partial pressure of carbon dioxide can then be calculated. Certain assumptions must be made as to the amount of free and hydrated carbon dioxide in solution, the degree of ionisation of the different electrolytes, and so on. Values for calcite which are of the same order of magnitude have been calculated by different authors and are recorded in the table on the following page.

The last value was obtained by recalculation from the data of McCoy and Smith, assuming that only a small part of the dissolved carbon dioxide is combined with water, and that, consequently, carbonic acid is a stronger acid than has previously been supposed.

[1] Johnston and Williamson, *J. Amer. Chem. Soc.*, 1916, **38**, 975. See table on p. 111.
[2] McCoy and Smith, *ibid.*, 1911, **33**, 468. See Bicarbonate.
[3] See for example, Ljubavin, *J. Russ. Phys. Chem. Soc.*, 1892, **24**, 389 ; Holleman, *Zeitsch. physikal. Chem.*, 1893, **12**, 125 ; Kohlrausch and Rose, *ibid.*, 1893, **12**, 234 ; Treadwell and Reuter, *Zeitsch. anorg. Chem.*, 1898, **17**, 170; Seyler and Lloyd, *Trans. Chem. Soc.*, 1909, **95**, 1347.
[4] Wells, *J. Wash. Acad. Sci.*, 1915, **5**, 617.
[5] Kohlrausch and Rose, *loc. cit.*
[6] Kendall, *Phil. Mag.*, 1912, [6], **23**, 958.
[7] See p. 108.

Temp., °C.	Sol. prod.	Authority.
16	2.84×10^{-9}	Bodländer, *Zeitsch. physikal. Chem.*, 1900, **35**, 23.
25	9.3×10^{-9}	McCoy and Smith, *J. Amer. Chem. Soc.*, 1911, **33**, 468.
16	9.8×10^{-9}	Johnston, *J. Amer. Chem. Soc.*, 1915, **37**, 2001.
25	7.19×10^{-9}	Seyler and Lloyd, *Trans. Chem. Soc.*, 1917, **111**, 994.
25	7.24×10^{-9}	Osaka, *J. Tokyo Chem. Soc.*, 1920, **41**, 453.

Johnston's formula for the relation between the solubility product of calcium carbonate and the partial pressure of carbon dioxide is,

$$nrK = \frac{[Ca^{\cdot\cdot}] \times [HCO_3']^2}{cP}$$

where " n " is the proportion of total carbon dioxide in the solution as carbonic acid, H_2CO_3, " r " is the ratio k_1/k_2, that is the ratio

$$\frac{[H^{\cdot}] \times [HCO_3']}{[H_2CO_3]} \Big/ \frac{[H^{\cdot}] \times [CO_3'']}{[HCO_3']},$$

" K " is the solubility product constant, and " cP " is the molar concentration of the dissolved gas, " P " being the partial pressure expressed in atmospheres, and $c = \frac{a}{22.4}$ where " a " is the absorption coefficient of carbon dioxide.

Using Wells' data, Johnston and Williamson also calculated the solubility product for different temperatures [1]:—

Temp., °C.	0	5	10	15	20	25	30
$K \times 10^9$.	12·2	11·4	10·6	9·9	9·3	8·7	8·1

The changes of solubility caused by slight variations in the carbon dioxide content of the atmosphere are of great importance geologically, for many natural waters are saturated with calcium carbonate, and alternate solution and deposition may bring about the transference of large quantities of it. The presence of other salts has also an important influence on the solubility. Ammonium salts, probably through the formation of a complex calcium-ammonium ion, can increase it to a considerable extent.[2] The solubility is, in general, increased by the presence of chlorides, nitrates, and sulphates, but decreased by alkali carbonates and alkaline earth salts. It is also increased in water containing humus, especially when alkali salts are also present.[3] In

[1] Johnston and Williamson, *J. Amer. Chem. Soc.*, 1916, **38**, 975.
[2] Drechsel, *J. prakt. Chem.*, 1877, [2], **16**, 169; Rindell, *Zeitsch. physikal. Chem.*, 1910, **70**, 452; Warynski and Kouropatwinska, *J. Chim. phys.*, 1916, **14**, 328; Bäckström, *Zeitsch. physikal. Chem.*, 1921, **97**, 179.
[3] Cameron and Seidell, *J. Physical Chem.*, 1902, **6**, 50; Gothe, *Chem. Zeit.*, 1915, **39**, 305, 326.

chloride solutions the solubility passes through a maximum.[1] Calcium carbonate is soluble in acids, with evolution of carbon dioxide.

A colloidal solution of calcium carbonate can be obtained by passing carbon dioxide into a suspension of calcium oxide in methyl alcohol. Ultimately a solid jelly, soluble in methyl alcohol, is obtained. It is miscible with benzene, chloroform, toluene, and ether, but is precipitated by acetone and carbon disulphide.[2]

The Hydrates of Calcium Carbonate.—By exposure of calcium saccharate to the air,[3] or to an atmosphere of carbon dioxide at 0° C.,[4] or by injecting carbon dioxide into an ice-cold sugar-lime solution through a capillary tube,[4] crystals of the hexahydrate, $CaCO_3.6H_2O$, formerly supposed to be the pentahydrate, are obtained. They may also be prepared by slow precipitation at 0° C.[5] In this case it is advisable to add a little potassium hydroxide, and the precipitate should be filtered, washed with alcohol and ether, and dried by suction as rapidly as possible.[6] The hexahydrate is thus obtained in colourless monoclinic crystals, which rapidly pass into calcite and water even when kept at 0° C. An attempt has been made by Mackenzie[4] to determine the transition temperature by means of the dilatometer, and it was found that below 5° C. the hydrate is fairly stable, but that, when the change has set in, lowering the temperature does not stop it. By boiling with absolute alcohol Pelouze obtained a trihydrate. According to Johnston and his co-workers only the hexahydrate exists, but Tschirwinsky described two mineral forms, trihydrocalcite, $CaCO_3.3H_2O$, and pentahydrocalcite, $CaCO_3.5H_2O$.[7]

Double Salts.—The best known, and most widely distributed, naturally occurring double carbonate of calcium is dolomite, or *bitter spar*, which may contain varying proportions of calcium to magnesium, and is, therefore, to be regarded as a solid solution rather than as a compound.[8] It forms yellow or white, massive, crystalline aggregates of density 2 8–2·95. It is harder than limestone, and less easily soluble in acids. It is sometimes used for building-stone. On heating to 400° C. it becomes capable of setting with water like cement.[9] Dolomite may be formed artificially by the action of ammonium carbonate on calcium and magnesium chlorides in an atmosphere of carbon dioxide.[10] Plumbocalcite has already been mentioned.

By the action of sodium carbonate solution on calcium hydroxide, *pirssonite*, $Na_2Ca(CO_3)_2.2H_2O$, *gaylussite*, $Na_2Ca(CO_3)_2.5H_2O$, or the anhydrous salt, $Na_2Ca(CO_3)_2$, may be formed, depending on the condi-

[1] Cameron and Robinson, *J. Physical Chem.*, 1907, **11**, 577.

[2] Neuberg and Rewald, *Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 820 ; *Biochem. Zeitsch.*, 1908, **9**, 537.

[3] Pelouze, *Ann. Chim. Phys.*, 1831, [2], **48**, 301 ; *Compt. rend.*, 1865, **60**, 429 ; Becquerel, *Ann. Chim. Phys.*, 1831, [2], **47**, 5 ; Salm-Horstmar, *Annalen*, 1835, **16**, 193 ; Rammelsberg, *Ber.*, 1871, **4**, 569.

[4] Mackenzie, *Trans. Chem. Soc.*, 1923, **123**, 2409.

[5] Pelouze, *Compt. rend.*, 1865, **60**, 429; Roth, *J. prakt. Chem.*, 1855, [1], **65**, 253 ; Vetter, *Zeitsch. Kryst. Min.*, 1911, **48**, 55.

[6] Johnston, Merwin, and Williamson, *Amer. J. Sci.*, 1916, [4], **41**, 473.

[7] Tschirwinsky, *Zeitsch. Kryst. Min.*, 1909, **46**, 302.

[8] Spangenberg, *ibid.*, 1913, **52**, 529 ; but see Mitchell, *Trans. Chem. Soc.*, 1923, **123**, 1055.

[9] Deville, *Compt. rend.*, 1865, **61**, 975 ; *Jahresber.*, 1865, 798 ; Crace-Calvert, *Compt. rend.*, 1865, **61**, 1168 ; *Jahresber.*, 1865, 798.

[10] Spangenberg, *loc. cit.*

tions of temperature and concentration.[1] Three double calcium potassium salts, $K_2Ca(CO_3)_2$, $K_6Ca(CO_3)_4$, and $K_6Ca_2(CO_3)_5.6H_2O$, have also been obtained.[2] The anhydrous double salts, $Na_2Ca(CO_3)_2$ and $K_2Ca(CO_3)_2$, may be prepared by fusion.[3]

A compound of calcium chloride with calcium carbonate has been described.[4]

By fusing together calcium and lithium carbonates in a current of carbon dioxide, a compound, probably of composition $CaCO_3.2Li_2CO_3$, is formed. It is readily decomposed by water.[5]

Basic Calcium Carbonate.—By heating quicklime in carbon dioxide Raoult obtained two compounds, to which he gave the formulæ $2CaO.CO_2$ and $3CaO.2CO_2$, and possibly also the compounds $4CaO.3CO_2$ and $5CaO.2CO_2$. The two former are hydrated and set like cement when treated with water, giving $CaCO_3.Ca(OH)_2$ and $2CaCO_3.Ca(OH)_2$.[6] The vapour pressure curve of calcium carbonate at high temperatures, however, hardly favours the view that a basic carbonate may be formed, nor yet that solid solutions of oxide in carbonate are possible.[7]

Uses.—The chief use of calcium carbonate is for the production of quicklime.[8] It can also be used wherever a cheap mild alkali is required.

Calcium carbonate, as well as lime, has a beneficial action on the soil apart from the neutralisation of the soil acids. It is more suitable for the lighter soils, but can also increase to some extent the permeability of heavy soils.[9] It increases the availability of nitrogen.[10]

Calcium Bicarbonate.—As has already been seen from McCoy and Smith's determinations of the solubility of calcium carbonate, calcium hydrogen carbonate as a solid phase only becomes stable under a pressure of about 15 atmospheres. It is evident, therefore, that under ordinary conditions it must be a very unstable compound.[11]

By precipitating calcium chloride with potassium, or, preferably, ammonium bicarbonate at 0° C., filtering, washing with ice-cold water saturated with carbon dioxide, and then with ice-cold alcohol and ether, and drying at 0° C., a compound is formed of composition corresponding to the formula $CaCO_3.1.75H_2CO_3$. The fine white powder first obtained

[1] Boussingault, *Pogg. Annalen*, 1826, **7**, 97; Wegscheider and Walter, *Monatsh*, 1907, **28**, 633; Wegscheider, *Annalen*, 1907, **351**, 87; Butschli, *J. prakt. Chem.*, 1907, [2], **75**, 556; Fritzsche, *ibid.*, 1864, [1], **93**, 339; Barre, *Compt. rend*, 1912, **154**, 279; Fedotiev, *Zeitsch. anorg. Chem.*, 1913, **32**, 341. See also Kremann, *Applications of Physico-Chemical Theory* (Constable & Co., Ltd.), translated by Potts, 1913.

[2] Butschli, *Chem Zentr.*, 1907, i, 1138; Barre, *loc. cit.*; Datta and Mukherjea, *Proc. Chem. Soc.*, 1913, **29**, 185.

[3] Le Chatelier, *Compt. rend*, 1894, **118**, 415; Niggli, *Zeitsch. anorg. Chem.*, 1919, **106**, 126.

[1] Fritzsche, *J. prakt. Chem.*, 1861, [1], **83**, 213.

[5] Lebeau, *Ann. Chim. Phys.*, 1905, [8], **6**, 437.

[6] Raoult, *Compt rend*, 1881, **92**, 189, 1457.

[7] See p. 109. Contrast Barium Peroxide.

[8] See p. 150.

[9] Engels, *Landw. Versuchs-stat.*, 1914, **83**, 408, see *J. Chem Soc.*, 1914, **106**, Abs. i, 468.

[10] Brown, *Centr. Bakt. Par.*, 1912, ii, **34**, 148, see *J. Chem. Soc.*, 1912, **102**, Abs. ii, 670; Lemmermann and Fresenius, *Bied. Zentr.*, 1912, **41**, 666, see *J. Chem. Soc.*, 1912, **102**, Abs. ii, 1206; Potter and Snyder, *Soil Science*, 1916, **1**, 76, see *J. Chem. Soc.*, 1916, **110**, Abs. i, 459; Blair and McLean, *Soil Science*, 1916, **1**, 489, see *J. Chem. Soc.*, 1916, **110**, Abs. i, 590.

[11] Keiser and Leavitt, *J. Amer. Chem. Soc.*, 1908, **30**, 1711; Keiser and McMaster, *ibid.*, 1714.

rapidly becomes pasty and evolves a considerable quantity of gas if the temperature is allowed to rise.[1]

If a solution of calcium bicarbonate which is just neutral to phenol-phthalein is analysed, its composition corresponds to the formula $CaCO_3.1\ 8H_2CO_3$,[2] but this is not necessarily any indication of the composition of the bicarbonate.

It is the presence of the acid carbonate of calcium which is the main cause of the temporary hardness of water.

Calcium Trithiocarbonate.—By the action of carbon disulphide on calcium hydrosulphide only double compounds of calcium trithio-carbonate and calcium hydroxide can be obtained, and not the simple salt.[3] From aqueous solutions reddish-yellow needles of the composition $3Ca(OH)_2.CaCS_3\ 9H_2O$ separate, and from alcoholic solutions similar needles corresponding with the formula $Ca(OH)_2.CaCS_3.2H_2O$. On acidifying a solution of either compound, one-third of the sulphur is evolved as sulphuretted hydrogen. Sulphur dissolves in the solution, forming a solution of perthiocarbonate.

Calcium Perthiocarbonate.—If a stream of hydrogen saturated with carbon disulphide vapour be passed through an aqueous solution of calcium polysulphide, and the solution evaporated *in vacuo*, dark red needles of composition $CaCS_4.2Ca(OH)_2.8H_2O$ are deposited.[4]

When alcoholic solutions are employed, addition of ether precipitates oils which take a long time to crystallise. These contain perthio-carbonate and also a large and varying amount of calcium thiosulphate. On drying *in vacuo*, or in a current of hydrogen, they decompose, leaving hydrated calcium polysulphides.

Calcium Cyanide, $Ca(CN)_2$, is obtained, in solution only,[5] by treating calcium hydroxide with a solution of hydrocyanic acid,[6] or by fusing calcium ferrocyanide out of contact with air and extracting with water.[7] Very dilute solutions are stable, but if concentrated above 15 per cent. they decompose rapidly, evolving ammonia and hydro-cyanic acid and precipitating lime. Owing to the hydrolysis of the cyanide, the solution has an alkaline reaction and a large partial pressure of hydrocyanic acid. Even so weak an acid as carbonic acid decom-poses the cyanide, liberating hydrocyanic acid.

A double calcium cuprous cyanide, $CaCu(CN)_3.4H_2O$, in prismatic needles,[8] and two calcium mercury salts, $CaHg_2(CN)_6.3H_2O$ (and $8H_2O$), in colourless hygroscopic needles, and $Ca_2Hg_3(CN)_{10}.6H_2O$, in leaflets,[9] have been described. There are also two calcium man-ganocyanides, $Ca_2Mn(CN)_6$ and $CaMn_2(CN)_6$, a manganicyanide, $Ca_3Mn_2(CN)_{12}$,[10] a crystalline double calcium silver cyanide, and an

[1] Keiser and Leavitt, *loc. cit.*

[2] Keiser and McMaster, *loc. cit.*

[3] Yeoman, *Trans. Chem. Soc*, 1921, **119**, 47. See also Sestini, *Gazzetta*, 1871, **1**, 473; Walker, *Chem News*, 1874, **30**, 28; Veley, *Trans. Chem. Soc.*, 1885, **47**, 478; O'Donoghue and Kahan, *ibid.*, 1906, **89**, 1812; Berzelius, *Pogg. Annalen*, 1826, **6**, 444.

[4] Yeoman, *loc. cit.*

[5] But see Basset and Germain, French Patent, 324232 (1902); *J. Soc. Chem. Ind.*, 1903 **22**, 554.

[6] Joannis, *Ann. Chim. Phys.*, 1882, [5], **26**, 482.

[7] Schulz, *J. prakt. Chem.*, 1856, [1], **68**, 257.

[8] Grossmann and von der Forst, *Zeitsch. anorg. Chem.*, 1905, **43**, 94.

[9] Grossmann and von der Forst, *Ber.*, 1904, **37**, 4141.

[10] Eaton and Fittig, *Annalen*, 1868, **145**, 157; Descamps, *Ann. Chim. Phys.*, 1881, [5], **24**, 178. For calcium platinocyanide, and ferro- and ferri-cyanides, see Vol. IX. of this series, Parts I. and II.

uncrystallisable calcium zinc cyanide. A compound, $Hg(CN)_2.Ca(CN)_2.$ $HgI_2.7H_2O$, is apparently immediately formed in solution on mixing mercuric cyanide and calcium iodide. The heat of formation is 49·5 Cal.[1]

Calcium Oxycyanide, $Ca(CN)_2.3CaO.15H_2O$, can be obtained by evaporating a solution of calcium cyanide *in vacuo* over sulphuric acid. The undissolved portion left when hydrocyanic acid is allowed to act upon an excess of milk of lime is the same product. It crystallises in small needles which are decomposed by water and alcohol.[2]

At atmospheric temperature gaseous hydrocyanic acid reacts with solid calcium hydroxide, producing the compound $3Ca(OH)_2.$ $2Ca(CN)_2.13H_2O.$[3]

Calcium Cyanamide, $CaCN_2$. — In 1895, after Moissan's and Willson's discovery[4] made practicable the preparation of carbides on a commercial scale, Frank and Caro attempted the fixation of atmospheric nitrogen by heating alkali or alkaline earth carbides to a sufficiently high temperature in free nitrogen. It was found that, whereas the alkalies gave cyanide, the barium compound contained a large proportion of cyanamide, and calcium formed cyanamide only, between 1100° and 1200° C. The discovery that calcium cyanamide could be used in agriculture as a nitrogenous fertiliser resulted in the rapid development of the cyanamide industry which began at Odda in 1908.[5]

Calcium carbide is used as the raw material instead of lime and coke because the temperature required for the formation of the carbide, which appears to be necessarily an intermediate product, is above the decomposition temperature of the cyanamide.[6]

The carbide is crushed to a fine powder, sieved, and packed in perforated steel retorts previously lined with corrugated paper. These are transferred to heat-insulated ovens lined with fire-brick and fitted with a carbon rod through the centre. The latter heats the furnace by the resistance it offers to an electric alternating current passed through it. When the necessary temperature is reached in the neighbourhood of the carbon rod, pure dry nitrogen is passed in and absorption begins in accordance with the equation—

$$CaC_2+N_2=CaCN_2+C.$$
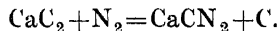
As the reaction is exothermic, the mass rapidly becomes incandescent, and an average temperature of 1100°–1200° C. is maintained until absorption is complete, but it must not be allowed to rise above about 1300°–1400° C., or the process will be reversed.[7] The decomposition

[1] Varet, *Compt. rend.*, 1895, **121**, 499.
[2] Joannis, *loc. cit.*
[3] Pincass, *Chem. Zeit.*, 1922, **46**, 347.
[4] See Calcium Carbide.
[5] Frank, *Zeitsch. angew. Chem.*, 1903, **16**, 536; 1906, **19**, 835; *J. Soc. Chem. Ind.*, 1908, **27**, 1093; *Trans. Faraday Soc.*, 1908, **4**, 99; Caro, *Chem. Trade J.*, 1909, **44**, 621; *Zeitsch. angew. Chem*, 1909, **22**, 1178; Erlwein, *Zeitsch. Elektrochem.*, 1906, **12**, 551; see also *Engineering*, 1914, **98**, 267.
[6] Rudolfi, *Zeitsch. anorg. Chem.*, 1907, **54**, 170; Kuhling, *Ber.*, 1907, **40**, 310; but see Erlwein, *Zeitsch. angew. Chem.*, 1903, **16**, 533; *J. Soc. Chem. Ind.*, 1903, **22**, 794; Cyanid-Gesellschaft, Berlin, English Patent, 16298 (1902); *J. Soc. Chem. Ind.*, 1903, **22**, 554; U.S. Patent, 757185 (1904), *ibid.*, 1904, **23**, 489; Bonnington and Akens, American Patent, 1021445 (1912), from Kohler, *Die Industrie der Cyanverbindungen* (Braunschweig), 1914, p. 115.
[7] Matignon, *Ann. Chim. Phys*, 1908, [8], **14**, 51; Le Blanc and Eschmann, *Zeitsch. Elektrochem.*, 1911, **17**, 20.

temperature varies with the purity of the carbide and the pressure of nitrogen.[1]

The process may be made either continuous or discontinuous. The nitrogen is obtained by the fractional distillation of liquid air or by passing air over heated copper. Heat may also be applied to the furnace by a gas flame.[2]

The cold product, containing about 20 per cent. of nitrogen, has a dark grey colour owing to the separated carbon. It is crushed, ground, and sprayed with a small quantity of water to decompose any unchanged carbide and slake any free lime. Finally, it is mixed with a little mineral oil to render it dustless. It is stated that sugar or similar solutions, derived from molasses or cellulose manufacture, are better than mineral oil for this purpose, as they combine with lime to form sucrates for example, which act as a binding agent for the dust and aid the action of the fertiliser by the development of bacteria.[3]

The total yearly production in 1913 was 150,000–160,000 metric tons, but in 1918 it had reached nearly 800,000 metric tons.

There are several trade names for calcium cyanamide indicating products of slightly varying composition :—

Lime nitrogen is the crude calcium cyanamide simply ground to a fine powder after removal from the oven. It contains about 55 per cent. calcium cyanamide, 2 per cent. calcium carbide, and about 20 per cent. free lime.

Cyanamid is the trade name for the completely hydrated material prepared for use as a fertiliser in the United States, America. It contains about 48 per cent. calcium cyanamide, 27 per cent. calcium hydroxide, and no carbide.

Nitrolim or *nitrolime* is the trade name for the material sold in England for agricultural purposes. It is lime nitrogen with just enough water to destroy the carbide, but practically all the free lime is present as calcium oxide.

Kalkstickstoff, the German commercial product, is similar to nitrolim.

Stickstoffkalk was formerly the crude calcium cyanamide made at Westeregeln by nitrifying calcium carbide containing about 10 per cent. of calcium chloride, according to Polzeniusz's process,[4] whereby the temperature of reaction is lowered.[1] Its manufacture was discontinued in 1910.

Calciocianamide is the carefully hydrated Italian commercial product.

Cyanamide de calcium is the corresponding French product.[5]

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[1] See p. 119.

[2] Allmand and Williams, *J. Soc. Chem. Ind.*, 1919, 38, 304R.

[3] Caro gives an account of a variety of methods suggested for removing causticity and dust, *Chem. Zeit.*, 1920, 44, 53 ; Stutzer, German Patent, 226340, see *Chem. Tech. Rep.*, 1910, 34, 527 ; Stutzer also suggested the addition of calcium nitrate and partial fusion by heating the mixture to 40° C., German Patent, 242164, *Chem. Tech. Rep.*, 1912, 36, 581, as well as the addition of inorganic colloids, German Patent, 242522, *ibid*, 1912, 36, 57.

[4] Polzeniusz, German Patent, 163320 (1901) ; *Chem. Zeit.*, 1907, 31, 958.

[5] For further details of manufacture, etc., see Pranke, *Cyanamid* (Williams & Norgate), 1913 ; Pring, *The Electric Furnace* (Longmans, Green & Co.), 1921, p. 131 ; Martin, *Industrial Chemistry, Inorganic* (Crosby Lockwood & Son), 1917, vol. i, p. 475 ; Thorpe, *Dictionary of Applied Chemistry* (Longmans, Green & Co.), 1912, vol. iii, p. 701 ; Williams, *Cyanogen Compounds* (Churchill), 1915, p. 264; "Calcium Carbide and Nitrogen Products," *Engineering*, 1914, 98, 267, 294, 351, 406, 465 ; Knox, *Fixation of Atmospheric Nitrogen* (Gurney & Jackson), 1914, p. 89.

The effect of the presence of various oxygen-free salts on the temperature of nitrogen absorption has been studied by several investigators.[1] Calcium chloride, which has a lower melting-point than calcium fluoride, is more effective in reducing the temperature of the reaction and thus accelerating it,[2] but a limit is reached. Sulphides, which have a high melting-point, are without influence.[3] Potassium carbonate accelerates the reaction, the optimum concentration at 900° C. being 4 per cent.[4] In general, bromides and iodides cause a greater acceleration than chlorides. Metals of low atomic weight have a greater influence than those of higher in the same periodic group.[5] Bredig regarded the accelerating action as simply due to partial fusion by which the protective coating of calcium cyanamide is removed, and the unchanged carbide exposed to the action of the nitrogen. This seems plausible, but Polzeniusz suggested that, with added calcium salts, there is intermediate formation of calcium nitride by the action of nitrogen on the ions of the added salt dissociated in the fused mixture.[3]

In connection with the influence of foreign salts on the rate of absorption, it is interesting to note that Moissan could observe no reaction between nitrogen and pure calcium carbide, at least up to 1200° C.[6]

Calcium cyanamide may also be obtained by fusing calcium cyanate,[7] or by fusing cyanamide, $CN.NH_2$, or urea,[8] with lime. It forms colourless crystals which sublime at 1050° C. at atmospheric pressure.[9]

The molecular heat of formation of calcium cyanamide from carbide diminishes with increasing temperature, as is seen from the following table [10] :—

Temperature, ° C.	1100	1200	1300	1400
Heat of formation in Cal.	63·9	27·0	18·8	15·2

The heat of formation from its elements is 94·820 Cal. if amorphous carbon be employed, or, if this be replaced by diamond, 91·480 Cal.[8]

As there are four phases present, three solid and one gaseous, and three components, the system is monovariant, and for every temperature there should be a definite dissociation pressure of nitrogen.[11] The following values have been found experimentally [12] :—

Temperature, ° C.	1053	1114	1160	1223	1278	1308	1378	1448
Pressure, cm. mercury	2·3	6·8	12·5	22·4	27·3	28·3	37·8	44·4

[1] Kühling, loc. cit.

[2] Carlson, Chem. Zeit , 1906, 30, 1261; Foerster and Jacoby, Zeitsch. Elektrochem., 1907, 13, 101; 1909, 15, 820; see also Rudolfi, Zeitsch. anorg. Chem , 1907, 54, 170.

[3] Polzeniusz, Chem. Zeit., 1907, 31, 958.

[4] Pollacci, Zeitsch. Elektrochem., 1908, 14, 565.

[5] Bredig, Fraenkel, and Wilke, ibid., 1907, 13, 69, 605.

[6] Moissan, Compt. rend., 1894, 118, 501.

[7] Drechsel, J. prakt. Chem., 1877, [2], 16, 200.

[8] Kameyama, J. Coll. Eng. Tokyo Imp. Univ., 1920, 10, 173, 209, 249, see J. Soc. Chem. Ind., 1920, 39, 818A, and Chem. Abs., 1921, 15, 1110.

[9] de Kay Thompson and Lombard, Met. Chem. Eng., 1910, 8, 682; Ehrlich, Zeitsch. Elektrochem., 1922, 28, 529, gives the sublimation temperature of the pure compound as 1300° C.

[10] de Kay Thompson and Lombard, loc. cit.; see also Dolch, Zeitsch. Elektrochem., 1920, 26, 455. Ehrlich gives the heat of the reaction $CaC_2 + N_2 = CaCN_2 + C$ as 61·4 Cal.

[11] le Blanc and Eschmann regarded the system as divariant, Zeitsch. Elektrochem., 1911, 17, 20; see also Ehrlich, ibid., 1922, 28, 529.

[12] de Kay Thompson and Lombard, Met. Chem. Eng., 1910, 8, 617, 682.

Kameyama found that the temperature at which the dissociation pressure of nitrogen is one atmosphere is 1754° C. if the carbon be present as graphite, or 1690° C. for amorphous carbon.[1]

The higher the pressure is raised above the dissociation pressure for any one temperature, the more readily will the formation of cyanamide take place at that temperature, but Pollacci found that a limit is reached at two atmospheres.[2]

Oxygen reacts with calcium cyanamide at 420°–450° C. with the formation of calcium carbonate and nitrogen. Below 1070° C. carbon dioxide gives calcium carbonate or calcium oxide according to temperature, and nitrogen, whilst above 1110° C. the separation of carbon takes place owing to the action of the carbon monoxide produced.

$$CaCN_2 + CO = CaO + 2C + N_2.$$
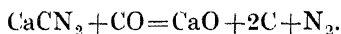
Carbon monoxide alone exerts no action on calcium cyanamide up to 1000° C.[3]

Calcium cyanamide is insoluble in alcohol but easily soluble in water, about 2·5 grm. dissolve in 100 c.c. of water at 25° C. It is hydrolysed by water, forming the acid salt $Ca(CN.NH)_2$. A basic salt, $(CaOH)_2CN_2.6H_2O$, has also been separated from solutions containing excess of lime,[4] and by passing carbon dioxide into a solution of calcium cyanamide a compound. $Ca(CN.N.CO_2).5H_2O$, is obtained.[1]

Two structural formulæ have been given for calcium cyanamide, one representing it as the calcium salt of cyanamide, $Ca=N-C\equiv N$, and

the other as the calcium salt of di-imide, $C \underset{\diagdown N}{\overset{\diagup N}{\diagup}} Ca$.[5]

Uses.—A crude cyanide mixture known as " surrogate," to be used for the extraction of metals from their ores, can be obtained by heating the commercial calcium cyanamide, which contains carbon, with sodium chloride,[6]

$$CaCN_2 + C + 2NaCl = CaCl_2 + 2NaCN,$$
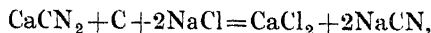
or, better still, with sodium carbonate, because the process is not reversible.[7] Calcium cyanamide may also be applied directly to the extraction of ores.[8]

Calcium cyanamide forms an intermediate product in one of the methods of fixing atmospheric nitrogen. By treating with superheated steam, ammonia is obtained [9]—

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$
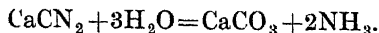
It may also be used as the starting-point for the preparation of a number of organic compounds. By the action of water and carbon

[1] Kameyama, *loc. cit.*
[2] Pollacci, *Zeitsch. Elektrochem.*, 1908, 14, 565.
[3] Kameyama, *loc. cit.*; see also Caro, *Zeitsch. angew. Chem.*, 1910, 23, 2405.
[4] Meyer, *J. prakt. Chem.*, 1878, [2], 18, 419 ; see also Milo, *Chem. Zentr.*, 1911, ii, 1655.
[5] Caro, *Zeitsch. anorg. Chem.*, 1909, 22, 1178.
[6] Erlwein, *5th Inter. Cong. Appl. Chem.*, 1903.
[7] Caro, *7th Inter. Cong. Appl. Chem.*, 1909; *Zeitsch. angew. Chem.*, 1909, 32, 1178.
[8] Clancy, *Met. Chem. Eng.*, 1910, 8, 608, 623 ; 1911, 9, 21, 53, 123 ; U.S. Patents, 976043, 976044, 976045 (1910); 1010347 (1911) ; *J. Soc. Chem. Ind.*, 1910, 29, 1459 ; 1912, 31, 32.
[9] Sulzer, *Zeitsch. angew. Chem.*, 1912, 25, 1268 ; Manuelli, *Annali Chim. Appl.*, 1914, 1, 388, see *J. Chem. Soc.*, 1914, 106, Abs. i, 812 ; Cyanid-Gesellschaft, *Zeitsch. angew. Chem.*, 1903, 16, 520.

dioxide in the cold, cyanamide is formed,[1] and by extracting with hot water, dicyano-diamide, $(H_2NCN)_2$, is obtained. The latter is used in the production of certain organic dyes and for reducing the temperature of combustion of explosives. By suitable treatment with dilute acids and a catalyst, urea, guanidine, and nitro-guanidine may be obtained.[2]

Calcium cyanamide also forms one of the constituents of the preparation " Ferrodur " used for case-hardening and tempering iron and steel.

Perhaps the most important use of nitrolime is as a fertiliser, but the fact that it may do serious harm if improperly used has caused it to fall into disfavour to some extent.[3] It should be applied to the soil at or before the time of sowing, and well distributed in not too large a quantity,[4] and not as a top dressing.[5] The nature of the soil should also be carefully considered. Nitrolime and its products do not readily disappear from clayey or sandy soils, but are decomposed in peaty soil.[6]

Nitrolime in too large quantities is toxic to plants, especially if it contains dicyanodiamide.[7] This compound is also destructive to nitrifying organisms, thus preventing the decomposition of the nitrolime from going further than the ammonia stage.[8] Humus-containing soils, however, apparently absorb dicyanodiamide to such an extent that the poisonous action disappears, and presumably the nitrogen becomes available for plant life.[9] Nitrolime may be used as a weed-killer if scattered on the leaves when wet.[10] In the presence of the free lime, dicyanodiamide is thus produced.

It is evident that it is important to know the amount of dicyanodiamide present in commercial calcium cyanamide. Caro and others have worked out methods of estimation which depend on the fact that cyanamide is precipitated by a salt of silver in presence of excess of ammonia, whilst silver dicyanodiamide is soluble, but may be precipitated in the filtrate by the addition of a solution of potassium hydroxide.

The fertilising value of nitrolime nitrogen is somewhat less than that of either nitric nitrogen or ammonium nitrogen,[11] but it has the advantage of forming a fine, dry, non-hygroscopic powder.

If used with mixed fertilisers, it is better with nitrates than with phosphates, which are said to be almost immediately reverted,[12] and

[1] Ulpiani, *Gazzetta*, 1908, **38**, ii, 358.

[2] Immendorff and Kappen, *J. Soc. Chem. Ind.*, 1912, **31**, 257, 795; Kappen, with Immendorff or Kraus, various patents, *ibid.*, 1912, **31**; Ulpiani, *Chem. Zentr.*, 1909, i, 1915.

[3] Campbell and Gow, *App. Chem. Reports*, 1920, **5**, 288; Baumann, *Chem. Zeit.*, 1920, **44**, 158. See, however, Harker, *Brit. Assoc. Rep.*, 1922, **90**, 419.

[4] Muntz and Nottin, *Compt. rend.*, 1908, **147**, 902.

[5] Remy, *Landw. Jahrb.*, **35**, [4], 114, see *J. Chem. Soc.*, 1908, **94**, Abs. ii, 220.

[6] Russell, *App. Chem. Reports*, 1920, **5**, 372; Grazia, *Chem. Zentr.*, 1908, ii, 1060; see also Stutzer, *Chem. Zeit.*, 1912, **36**, 1141.

[7] von Seelhorst and Muther, *J. Landw.*, 1905, **53**, 329, see *J. Chem. Soc.*, 1906, **90**, Abs. ii, 47; Reis, *Biochem. Zeitsch.*, 1910, **25**, 477; Pfeiffer and Simmermacher, *Landw. Versuchs. Stat.*, 1917, **90**, 415, see *J. Soc. Chem. Ind.*, 1918, **37**, 67A.

[8] Russell, *App. Chem. Reports*, 1918, **3**, 347; Cowie, *J. Agric. Sci.*, 1919, **9**, 113, see *J. Chem. Soc.*, 1919, **116**, Abs. i, 376.

[9] Linter, *Bied. Zentr.*, 1919, **48**, 414, see *Chem. Abs.*, 1920, **14**, 1727.

[10] Pranke, *Cyanamid* (Williams & Norgate), 1913, chap. ix.

[11] Baessler, *Bied. Zentr.*, 1911, **40**, 302, see *J. Chem. Soc.*, 1911, **100**, Abs. ii, 650; Russell, *J. Soc. Chem. Ind.*, 1920, **39**, 5R.

[12] Hendrick, *J. Soc. Chem. Ind.*, 1911, **30**, 522.

which may also cause the rapid formation of dicyanodiamide.[1]   This, however, is contradicted by Pranke,[2] and nitrolime is apparently often used in conjunction with superphosphates.[3]   Mixed with nitrates, it checks their too rapid decomposition, increases their availability, and secures a more lasting and uniform effect.[4]   The resulting dilution of the cyanamide is also beneficial.

The first stage in the absorption of nitrolime by the soil is the removal of free lime by the action of carbon dioxide.   By a complex process, which is variously ascribed to the agency of colloids,[5] ferric oxide,[6] zeolites,[7] or bacteria,[8] urea is produced, and, by bacterial action, is ultimately transformed, first into ammonium salts, and finally into nitrates.[3]

Calcium Cyanate, $Ca(CNO)_2$, may be prepared in the electric furnace by heating together limestone and carbon, first at 1500° C., then at 2500° C., in presence of nitrogen, and, finally, at the latter temperature in a current of air.   It is obtained in solution by passing the vapour of cyanic acid into milk of lime, but cannot be separated by crystallisation.[9] It has been proposed as a nitrogenous manure.[10]

Calcium Cyanurate, $Ca[H_2(CNO)_3]_2.8H_2O$, forms colourless needles sparingly soluble in hot water.[11]

Calcium Thiocyanate, $Ca(CNS)_2$, may be prepared synthetically by heating a 20-per-cent. ammonia solution in an autoclave with carbon disulphide and lime,

$$2NH_3 + 2CS_2 + 2Ca(OH)_2 = Ca(CNS)_2 + CaSO_4.$$
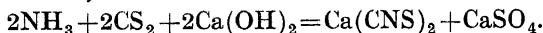
The sulphuretted hydrogen may be removed by carbon dioxide and the carbonate by filtration.[12]   It can also be prepared by the action of thiocyanic acid on calcium carbonate,[13] or by boiling cuprous or ammonium thiocyanate with lime and passing carbon dioxide through the solution to remove excess of lime.   The salt crystallises from aqueous solution with difficulty.   The formula of the crystals is $Ca(CNS)_2.3H_2O$, and they are very deliquescent and soluble.   The saturated solution boils at 143° C., and has an action on paper similar to that produced by caustic soda solution.[14]

It forms a series of double salts with the heavy metal thiocyanates, and with mercuric cyanide it gives crystals of the compound $Ca(CNS)_2.2Hg(CN)_2.8H_2O$.[15]

Calcium Selenocyanate has been obtained in crystalline needles.[16]

[1] Harger, *Chem. Met. Eng.*, 1920, **23**, 693.
[2] Pranke, *ibid.*, 1920, **23**, 1102.
[3] Russell, *App. Chem. Reports*, 1919, **4**, 368.
[4] Lumia, *Atti. R. Accad. Lincei*, 1914, [5], **23**, ii, 659.
[5] Ulpiani, *Gazzetta*, 1910, **40**, i, 613 ; Henschel, *Centr. Bakt. Par.*, 1912, ii, **34**, 279, see *J. Chem. Soc.*, 1913, **104**, Abs. i, 240 ; Lohnis, *ibid.*, 1915, **108**, Abs. i, 656.
[6] Reis, *Biochem. Zeitsch.*, 1910, **25**, 460, 477 , Stutzer and Reis, *J. Landw.*, 1910, **58**, 65, see *J. Chem. Soc.*, 1910, **98**, Abs. ii, 537 ; Stutzer, *Chem. Zeit.*, 1912, **36**, 1141.
[7] Cowie, *J. Agric. Sci.*, 1920, **10**, 163.
[8] Kappen, *Centr. Bakt. Par.*, 1909, ii, **24**, 382, see *J. Chem. Soc*, 1909, **96**, Abs. ii, 822 ; Mazé, Vila, and Lemoigne, *Compt. rend.*, 1919, **169**, 921.
[9] Williams, *Cyanogen Compounds* (Churchill), 1915, p. 174.
[10] Faure, *Compt. rend.*, 1895, **121**, 463.
[11] Williams, *Cyanogen Compounds* (Churchill), 1915, p. 178.
[12] Brock, Hetherington, Hurter, and Raschen, English Patent, 21451 (1893), see *J. Soc. Chem. Ind.*, 1894, **13**, 1195.
[13] Meitzendorff, *Pogg. Annalen*, 1842, **56**, 70.
[14] Williams, *Cyanogen Compounds* (Churchill), 1915, p. 196.
[15] Böckmann, *Annalen*, 1837, **22**, 153 ; Clève, *Bull. Soc. chim.*, 1875, [2], **23**, 71.
[16] Crookes, *J. Chem. Soc.*, 1852, **4**, 19.

CALCIUM AND SILICON.

Calcium Silicide, CaSi$_2$.—This compound was first obtained by Wöhler, by heating together a mixture of calcium chloride, metallic sodium, and sodium fluosilicate or crystallised silicon.[1]   It may be prepared by heating together in the electric furnace, lime or calcium carbonate with quartz and coal,[2] lime and silicon,[3] calcium chloride and silicon,[4] lime and silicon with the addition of calcium fluoride or chloride,[5] by direct combination of metallic calcium with silicon,[6] or, finally, by heating together calcium hydride and silicon at 1000°–1010° C. in an atmosphere of hydrogen.[7]

Calcium silicide forms a grey crystalline mass with a metallic lustre, and of the hardness of quartz.   Its heat of formation is 208·7 Cal.,[7] and its density is 2·5.   It is unaffected by hydrogen at red heat, but readily attacked by halogens.   It is slowly attacked by water giving calcium hydroxide, silica, and hydrogen.   With hydrofluoric acid it becomes incandescent.   When exposed to the air it is slowly oxidised, forming silica and lime.   Concentrated hydrochloric acid reacts with it, giving a silicone, $Si_3H_3O_2$, but with the dilute acid, hydrogen silicide is obtained, whilst alkalies produce pure hydrogen.[8]

Goldschmidt proposed the use of a mixture of calcium and calcium silicide in thermite reactions.[9]   If calcium silicide be added to a molten bath of iron or steel it acts as a deoxidising agent, and, owing to the heat of the reaction, as a reheater.[10]

Calcium Monosilicide, Ca$_2$Si$_2$.—Indications of the existence of another silicide have several times been observed.[11]   The formula Ca_3Si_2 has been ascribed to a compound obtained by heating together powdered silicon and calcium filings in the proper proportions at 1000° C.[12] It seems probable, however, that the true composition is represented by the formula, Ca_2Si_2.[7]

This compound gives spontaneously inflammable silicon hydride with dilute mineral acids, leaving a residue of hydrated silica.   With concentrated acids there is a slow evolution of hydrogen.   It is attacked by ammonia, and more readily by hot water than by cold.   By heating with hydrogen, practically pure disilicide, mixed with calcium hydride,

[1] Wöhler, *Annalen*, 1863, **125**, 255 ; **127**, 257.

[2] de Chalmot, *Amer. Chem. J.*, 1896, **18**, 319 ; Jacobs, *Brit. Assoc. Rep.*, 1900, 699 ; Bradley, *Chem. News*, 1900, **82**, 149.

[3] Moissan, *Compt. rend.*, 1898, **127**, 584 ; Moissan and Dilthey, *ibid.*, 1902, **134**, 503 ; *Ann Chim. Phys.*, 1902, [7], **26**, 289.

[4] Jungst and Mewes, German Patent, 167615, *Chem Zentr.*, 1905, i, 194.

[5] Goldschmidt, *Chem. Zentr.*, 1908, ii, 271.

[6] Honigschmid, *Monatsh.*, 1909, **30**, 497.

[7] Wöhler and Muller, *Zeitsch. anorg. Chem.*, 1921, **120**, 49.

[8] Moissan and Dilthey, *loc. cit.* ; Honigschmid, *loc. cit.*

[9] Goldschmidt, *Zeitsch. Elektrochem.*, 1908, **14**, 558 ; see also Watts and Breckenridge, *J. Soc. Chem. Ind.*, 1908, **27**, 752 ; Berger, *Compt. rend.*, 1920, **170**, 1492 ; **171**, 29.

[10] Anderson, *Raw Material*, 1921, **4**, 51, see *Chem. Abs.*, 1921. **15**, 3603.   See also Vickers, *Metals and their Alloys* (Crosby Lockwood & Son), 1923, p. 46.

[11] Le Chatelier, *Bull. Soc. chim.*, 1897, [3], **17**, 793 ; Tamaru, *Zeitsch. anorg. Chem.*, 1909, **62**, 81 ; see also Kolb, *ibid*, 1909, **64**, 342 ; but see Hönigschmid, *ibid.*, 1910, 66, 414.

[12] Hönigschmid, *Monatsh.*, 1909, **30**, 497 ; Hackspill, *Bull. Soc. chim.*, 1908, [4], **3**, 619.

is formed. At 1050° C. the monosilicide, in the absence of air, dissociates into the disilicide and calcium.

The density of the monosilicide, mixed with a little uncombined silicon, is 2·346. The heat of formation is 166·3 Cal.[1]

Calcium Silicalcyanide, Ca(SiAl)₂.—This compound is regarded by Reynolds[2] as analogous to calcium cyanide, silicon taking the place of carbon, and aluminium of nitrogen.[3] It may be obtained by the action of calcium, in small portions at a time, on a fused mixture of silicon and aluminium. After cooling, a dark grey mass showing brilliant crystalline faces remains. It is readily attacked by solutions of sodium and potassium hydroxides and by hydrochloric acid, slowly by boiling nitric acid, and not at all by hot sulphuric acid. Oxygen has not much action until the temperature of the oxyhydrogen flame has been reached, but, if heated to low redness in a stream of moist oxygen, the compound is converted into a white mass of the same composition as the mineral anorthite, $CaAl_2Si_2O_8$.[2]

Calcium Silicates.[4]—**Monocalcium Silicate or Calcium Metasilicate, $CaSiO_3$,** is found in nature as the mineral *wollastonite*, generally in calcareous rocks in volcanic regions. There is also a double calcium magnesium silicate, *diopside*, $CaSiO_3.MgSiO_3$,[5] and a hydrated form, *plombierite*, $CaSiO_3.H_2O$. Calcium metasilicate, in addition, takes part in the formation of a number of polybasic silicates. It is also produced during the crystallisation or devitrification of certain acid slags or of ordinary glass.[6]

It can be prepared by heating together lime and silica with, or without, calcium chloride,[7] or a mixture of calcium and sodium chlorides,[8] or in the wet way by the action of potassium silicate on calcium acetate.[9] Lime and precipitated silica begin to react at 1011° C., but the reaction is more vigorous above 1400° C.[10]

The natural compound has not the same optical characters as the artificial.[11] Both crystallise in the monoclinic system, but the artificial compound is pseudo-hexagonal, and the name pseudo-wollastonite is given to it. The two are also distinguished as α- (artificial) and β-metasilicate.

Wollastonite is stable below about 1200° C.,[12] and pseudo-wollastonite above. The transformation of the former into the latter is easily observed, but the reverse change is never obtained by simple cooling. Certain substances, however, catalyse the transition from the α- to the β-form, probably by acting as a solvent, for example, excess of calcium

[1] Wohler and Muller, *loc. cit.*
[2] Reynolds, *Proc. Roy. Soc.*, 1913, 88A, 37.
[3] It may also, perhaps, be regarded as a calcium alumino-silicide, especially in view of its oxidation product, but Reynolds considers that this is unlikely because of the unreadiness of aluminium and silicon to combine with one another.
[4] See Le Chatelier, *La Silice et les Silicates* (Hermann et Fils), 1914.
[5] Allen, White, Wright, and Larsen, *Amer. J. Sci.*, 1909, [4], 27, 1.
[6] Bourgeois, *Ann. Chim. Phys.*, 1883, [5], 29, 433.
[7] Lechartier, *Compt. rend.*, 1868, 67, 41.
[8] Gorgeu, *ibid.*, 1884, 99, 256.
[9] Becquerel, *ibid.*, 1874, 79, 82.
[10] Hedvall, *Zeitsch. anorg. Chem.*, 1916, 98, 57.
[11] Bourgeois, *loc. cit.*; Allen, White, and Wright, *Amer. J. Sci.*, 1906, [4], 21, 89.
[12] Day and Shepherd, *J. Amer. Chem. Soc.*, 1906, 28, 1089; Allen, White, and Wright, *loc. cit.*; Doelter, *Zeitsch. Kryst. Min.*, 1914, 54, 398; Day and Sosman, *Amer. J. Sci.*, 1911, [4], 31, 341; Ferguson and Merwin, *ibid.*, 1919, [4], 48, 165.

oxide or silica, calcium vanadate,[1] or calcium fluoride.[2] The transition apparently produces no thermal effect.[3]

The density of wollastonite is 2·919,[1] and of pseudo-wollastonite 2·914.[5] Values ranging from 1500°–1540° C. have been given for the melting-point of pseudo-wollastonite by different investigators,[6] but, according to Doelter, these are all too high, due to a lag in the determinations, and the true value lies between 1310° and 1380° C.[7] Leitmeier also obtained a low value and found that it varies with the size of the particles. The melting of fine grains begins at 1350° C., the whole becoming liquid at 1410° C., whilst coarse grains begin to melt at 1420° C.[8]

Doelter found a metastable melting-point for wollastonite between 1240° and 1320° C.[7]

The molecular heat of formation of calcium metasilicate from silica and calcium oxide is 16·1 Cal.[9] The specific heat of wollastonite is 0·178.[10]

By preparation in the wet way a monohydrate, $CaSiO_3.H_2O$, has been isolated,[11] and the anhydrous salt also hydrates when treated with lime water for some weeks, but it loses its water of hydration on drying at 100° C.[12] A hydrate, $CaSiO_3.2·5H_2O$, is mentioned by Le Chatelier.[13]

A study of the freezing-point curves of mixtures of sodium and calcium metasilicates indicates the existence of two compounds, $2Na_2SiO_3.3CaSiO_3$ and $3Na_2SiO_3.2CaSiO_3$.[14] With barium silicate a compound, $2CaO.BaO.3SiO_2$, is formed.[15] Freezing-point curves have also been given for mixtures of calcium metasilicate with calcium fluoride,[2] chloride,[3] and sulphide,[16] and with ferrous,[17] magnesium,[18] aluminium,[19] manganese,[4] lithium,[20] and titanium silicates.[21]

Dicalcium Silicate, or Calcium Orthosilicate, $2CaO.SiO_2$ or Ca_2SiO_4, does not occur in nature but is obtained by fusing together silica and calcium oxide in suitable proportions, or by dissolving

[1] Allen, White, and Wright, *loc. cit.*
[2] Tursky, *Zeitsch. anorg Chem.*, 1913, 82, 315.
[3] Karandéeff, *ibid.*, 1910, 68, 188.
[4] Ginsberg, *ibid.*, 1908, 59, 346.
[5] Allen, White, and Wright, *loc. cit.* ; Le Chatelier, *loc. cit.*
[6] Smolensky, *Zeitsch. anorg. Chem.*, 1912, 73, 293 ; Lebedeff, *ibid.*, 1911, 70, 301 ; Day and Shepherd, *J. Amer. Chem. Soc*, 1906, 28, 1089 , Ginsberg, *loc. cit.* ; Rankin and Wright, *Zeitsch. anorg. Chem.*, 1915, 92, 213 ; Wallace, *ibid*, 1909, 63, 1 ; Konstantinov and Selivanov, *Chem. Zentr.*, 1915, ii, 778 ; Karandéeff, *loc cit*
[7] Doelter, *loc. cit.*
[8] Leitmeier, *Zeitsch. anorg. Chem.*, 1913, 81, 209.
[9] Le Chatelier, *La Silice et les Silicates* (Hermann et Fils), 1914, p. 52.
[10] Kopp, *Annalen Suppl.*, 1864–5, 3, 295.
[11] Jordis and Kanter, *Zeitsch. anorg. Chem.*, 1903, 35, 82.
[12] Benzian, *Chem. Zeit.*, 1905, 29, 737.
[13] Le Chatelier, *Bull. Soc. chim.*, 1884, [2], 42, 82.
[14] Kultascheff, *Zeitsch. anorg. Chem.*, 1903, 35, 187.
[15] Eskola, *Amer. J. Sci.*, 1922, [5], 4, 331.
[16] Lebedeff, *loc. cit.*
[17] Konstantinov and Selivanov, *loc. cit.*
[18] Bowen, *Amer. J. Sci.*, 1914, [4], 38, 207 ; Ferguson and Merwin, *loc. cit.* ; Deleano, *Zeitsch. anorg. Chem.*, 1914, 84, 401
[19] Deleano, *loc. cit.*
[20] Wallace, *loc. cit.*
[21] Smolensky, *Zeitsch. anorg. Chem.*, 1912, 73, 293.

silica, alone or with calcium oxide, in calcium chloride.[1] It is frequently produced in slags on which it confers its own property of disintegrating on cooling.[2] It is a polymorphic compound. α-Orthosilicate melts at 2080° C., crystallises in the monoclinic system, has a density of 3·27, and hardness 5–6. By slow cooling it changes at 1410° C. to the orthorhombic β-compound, of density 3·28, and at 675° C. to the monoclinic γ-compound which has a decidedly smaller density, namely, 2·97. The last change must therefore involve a considerable increase in volume, and it is this increase which causes the pulverisation on slow cooling noticed by Le Chatelier. Rapid cooling fixes α-orthosilicate at the ordinary temperature.[3] There is also a fourth unstable form, β'-orthosilicate, obtained by cooling hydrated orthosilicate from 1425° C.[4] α-Orthosilicate has the power of setting with water, but this property is not possessed by the γ-variety. The β-compound cannot be kept at ordinary temperatures.

The tendency to form the γ-orthosilicate, and therefore to pulverise, can be reduced by the presence of certain foreign substances, for example, magnesium, aluminium, and iron oxides. It has been suggested that the difference between hydraulic and non-hydraulic dicalcium silicate is to be accounted for by a difference in the structure of the molecule,

the latter being a true orthosilicate, $Ca{<}{\overset{O}{\underset{O}{}}}{>}Si{<}{\overset{O}{\underset{O}{}}}{>}Ca$, and the former

a basic metasilicate, $SiO{<}{\overset{OCa}{\underset{OCa}{}}}{>}O$, which is readily hydrolysed, yielding

lime and normal metasilicate.[5]

The heat of formation from the metasilicate is 8·7 Cal., or from silica and lime 24·8 Cal.[6] The orthosilicate is more readily attacked by acid than the metasilicate.

With manganese orthosilicate in varying proportions a continuous series of solid solutions is formed.[7] With calcium chloride a compound, $2CaO.SiO_2.CaCl_2$, is obtained.[8] The freezing-point curve of binary mixtures of lithium and calcium orthosilicates indicates a compound $Li_4SiO_4.Ca_2SiO_4$, stable below 932° C. and of density 2·847.[9]

Tricalcium Silicate, $3CaO.SiO_2$.—The existence or otherwise of tricalcium silicate has been in the past the subject of much discussion, earlier investigators being rather in favour of regarding it as a mixture or solid solution of the orthosilicate and calcium oxide.[10] Recent work,

[1] Arndt and Loewenstein, *Zeitsch. Elektrochem.*, 1909, 15, 784.
[2] Le Chatelier, *Ann. Mines*, 1887, [8], 11, 392.
[3] Le Chatelier, *loc. cit.* ; *J. Soc. Chem. Ind.*, 1888, 7, 567, 847 ; Erdmenger, *ibid.*, 1893, 12, 834, 1035 ; Newberry and Newberry, *ibid*, 1897, 16, 887 ; Day and Shepherd, *J. Amer. Chem. Soc.*, 1906, 28, 1089 ; Day, Allen, Shepherd, White, Wright, and Tschermak, *Min. Pet. Mitt.*, 1907, [2], 26, 169 ; Shepherd and Rankin, *Zeitsch. anorg. Chem.*, 1911, 71, 19.
[4] Shepherd and Rankin, *loc. cit.*
[5] Zulkowski, *Chem. Ind.*, 1898, 21, 69, 96, see *J. Soc. Chem. Ind.*, 1898, 17, 353 ; *Chem. Ind.*, 1901, 24, 290, 317, 345, 369, 420, 445, see *J. Soc. Chem. Ind.*, 1901, 20, 990.
[6] Le Chatelier, *loc. cit.* ; *La Silice et les Silicates* (Hermann et Fils), 1914.
[7] Kallenberg, *Zeitsch. anorg. Chem.*, 1914, 88, 355.
[8] Le Chatelier, *Compt rend.*, 1883, 97, 1510 ; Gorgeu, *ibid.*, 1884, 99, 256
[9] Schwarz and Haacke, *Zeitsch. anorg. Chem*, 1921, 115, 87.
[10] Day and Shepherd, *J. Amer. Chem. Soc.*, 1906, 28, 1089 ; Zulkowski, *loc. cit.*

however, seems to have established its claim to be regarded as a chemical individual.[1]

Tricalcium silicate cannot be obtained by simple fusion of the constituents. Perhaps it is unstable at the melting-point, about 1700° C. It can, however, be prepared in the presence of small quantities of other oxides, for example, aluminium, boron, and chromium oxides,[2] which probably act as a flux,[3] allowing the reaction to take place at a lower temperature. It can also be prepared by heating the constituents for some time below the melting-point.

It is hydraulic and will hydrate and harden with water.

Acid Calcium Silicate, $CaSiO_3.H_2SiO_3.H_2O$, is found naturally as the mineral *okenite*. A substance of the same composition has been formed by precipitating calcium chloride with sodium silicate.[4] Gelatinous silica combines with lime-water, forming insoluble silicates of varying composition.[5]

Calcium Fluosilicate, $CaSiF_6$, is obtained in a vitreous or crystalline form by heating lime in a current of silicon fluoride.[6] It may be obtained as the crystalline dihydrate, $CaSiF_6.2H_2O$, by dissolving lime or calcium carbonate[7] in hydrofluosilicic acid and evaporating. It is decomposed by water forming calcium fluoride and silicic acid, and by heat forming silicon fluoride. It is easily soluble in 60 per cent. alcohol. The crystals belong to the monoclinic system.

GLASS.

Certain of the metallic silicates, especially alkali silicates, show a remarkable tendency to super-cool, giving a transparent structureless solid, known as a glass, which may be regarded as a liquid in a highly viscous condition. The alkaline earth silicates, aluminium silicate, and others, do not possess this property, or only to a very limited degree, extremely rapid cooling being necessary to obtain them in a vitreous condition. The silicates of iron, manganese, and lead do not readily crystallise unless cooled slowly. By mixing together silicates of the alkaline earths with the more readily crystallisable silicates, glasses are easily obtained which are at the same time capable of resisting the action of water and chemical reagents as the alkali silicates alone cannot do. In this possibility lies the foundation of the glass industry.

Glass of a very imperfect type was produced and employed as early as 1400 B.C., and probably before, in Syria and in Egypt, but it was not until the time of the Roman Empire that glass became an article of general domestic and industrial use. Roman glass was almost in-

[1] Newberry and Smith, *J. Soc. Chem. Ind.*, 1903, **22**, 94; Newberry and Newberry, *loc. cit.*; Richardson, *Tonind. Zeit.*, 1903, **27**, 942, see *J. Soc. Chem. Ind.*, 1903, **22**, 997; Le Chatelier, *La Silice et les Silicates* (Hermann et Fils), 1914, p. 426; Klein and Phillips, *Trans. Amer. Ceramic Soc.*, 1914, **16**, 313, see *J. Soc. Chem. Ind.*, 1914, **33**, 1052; Campbell, *J. Ind. Eng. Chem.*, 1914, **6**, 706, see *J. Soc. Chem. Ind.*, 1914, **33**, 964; Bates, *Trans. Amer. Ceramic Soc.*, 1913, **15**, 420, see *J. Soc. Chem. Ind.*, 1914, **33**, 81; Neumann, *Stahl und Eisen*, 1918, **38**, 953; Ferguson and Merwin, *Amer. J. Sci*, 1919, **48**, 81.

[2] Bates and Klein, *J. Franklin Inst.*, 1916, **182**, 398, see *J. Soc. Chem. Ind.*, 1916, **35**, 1016.

[3] Neumann, *loc. cit.*

[4] Heldt, *J. prakt. Chem.*, 1865, [1], **94**, 129, 157, see *Jahresber.*, 1865, 193

[5] Landrin, *Compt. rend.*, 1883, **96**, 841.

[6] Deville, *ibid.*, 1861, **52**, 782.

[7] Marignac, *Ann. Mines*, 1859, [5], **15**, 221.

variably of the soda-lime type, rich in silica. After the collapse of the Roman Empire, the Emperor Constantine encouraged the construction of glass furnaces at Byzantium, and these became celebrated throughout the civilised world until, after the taking of Constantinople in 1453, their products were eclipsed in beauty and delicacy by the work of the Venetian glass-blowers. The latter held first place for several centuries, until, in fact, in spite of stringent laws to prevent it, their secrets became known in England, France, and Germany. The Venetians, no doubt, owed part of their superiority in glass manufacture to the natural sodium carbonate which they imported and used. In other countries during mediæval times the manufacture degenerated, owing to the use of crude wood ashes and the production of a potash-lime glass, very low in silica and with an excess of lime and magnesia. So far as is known, the first English glass factory, if we except those put up during the Roman occupation and one probably conducted by French workmen brought by St. Wilfred to York about 700 A.D., was erected at Chiddingfold in Surrey about the year 1230, and this district remained the only centre of glass manufacture until restrictions on the use of timber for fuel in the time of Elizabeth caused its decline. The fashion for ornamental glass vessels, which prevailed in the sixteenth century, resulted in the establishment, in London and other parts of England, of glass-blowers from France and the Low Countries, as well as a few from Italy. The introduction of coal as a fuel, and the necessity for covering the pots to protect from contamination by the coal, facilitated the use of lead oxide in glass and led ultimately to the manufacture of lead or flint glass in the form now known.[1]

The composition of glass is varied according to the use to which it is to be put. Comparatively small changes in the composition may bring about rather serious changes in properties, and much experimental research has been necessary, and is still required, to discover suitable formulæ for glasses for special purposes. Before the War, the manufacture of chemical glass-ware and optical glass was developed on the Continent, but not in Britain. Since then, however, British manufacturers have made remarkable progress.[2]

Ordinary soda-lime glass approximates substantially to the composition $Na_2O.CaO.6SiO_2$, but there are very large possibilities of variation by replacing more soda by lime, exchanging soda for potash, or lime for baryta, magnesia, lead oxide, zinc oxide, or alumina, or, finally, by exchanging silica for phosphoric or boric acids. Small quantities of other substances may also be introduced, with the object of aiding in the refining of the glass or of producing coloured or opaque glass.

The earliest pioneers in the systematic study of glass, largely for optical and chemical purposes, were Schott and Abbe, who began their work in 1881, and set up a factory at Jena in 1884.[3]

The Manufacture of Glass.—The silica is introduced in the form of white sand, large quantities of which are obtained from Paris and Belgium. Flints were formerly employed to avoid the use of sand containing iron, hence the name "flint glass," but this has been discontinued. Lime may be introduced as slaked lime, chalk, or limestone,

[1] See Manufacture of Glass.
[2] Turner, Presidential Address, *J. Soc. Glass Tech.*, 1922, 6, 108.
[3] Hovestadt, *Jena Glass and its Scientific and Industrial Applications*, 1900, English translation by Everett and Everett (Macmillan & Co., Ltd.), 1902.

and soda chiefly as sodium sulphate, although carbonate is sometimes used. " Cullet," or waste glass, is also added to hasten the reaction by acting as a flux. The finely ground materials are mixed with a wooden shovel or a mixing machine, and introduced little by little into a previously heated pot. The actual melting occupies ten to twelve hours, depending on the quantity of glass and the type of furnace. There is a large evolution of gas, chiefly carbon dioxide and water vapour, which helps in the mixing, and a froth or scum is formed on the surface and is removed. This scum, known as " sandiver " or " glass gall," consists chiefly of sodium and calcium sulphates with a certain amount of glass. The glass is then refined or planed. Sometimes potatoes or apples are thrown in, or it is stirred with a stick of green wood at the end of which a fire-clay cylinder is attached. At the beginning of this process the glass should be intensely heated so as to be very fluid and mobile. The temperature sinks during the stirring, so that the glass is finally quite viscous, when it is ready for drawing and blowing.

Several pots are heated in one furnace, or, for the coarser kinds of glass, a single large tank may be used. Lead glass and optical and other special glasses must be melted in covered pots, to prevent access of reducing gases in the case of lead glass, or the dropping in of brick-work or other impurities from the roof of the furnace. The glass cannot then be stirred, but it must be removed, broken up, and the cleanest fragments returned to the pot for remelting in order to produce a homogeneous mass.

Great care must be exercised in the construction of both pots and furnace, as they must be capable of withstanding for some months at a time the action of a corrosive mixture at a temperature which may reach 1400° C. or even more.[1] A highly refractory clay, for example Stourbridge clay, consisting mainly of aluminium silicate, is used. The pots must be carefully annealed, and, when once heated up, must never be allowed to cool down again.

Gas-fired furnaces, being more economical than coal-fired ones, are more frequently used. There are also several types of electric furnace, for example the Sauvageon, Voelker, and Becker furnaces, in which the heat is developed by the resistance of the glass itself, or, on the other hand, those in which the furnace chamber is heated by the passage of an electric current through resistant material surrounding it.[2]

There is scope for much greater economy in the working of glass furnaces. Travers has calculated that, in three different glass furnaces, the heat energy actually utilised in melting the glass was 14·5, 12, and 9 per cent. respectively of the total consumed.[3] The rest was lost either outside the furnace or through the walls.

For fuller details of the processes of manufacture and the construction of furnaces and of machinery for the drawing and blowing of glass the reader is directed to the literature mentioned in the subjoined references.[4]

[1] Jenkinson, *J. Soc. Glass Tech.* 1918, 2, 288.

[2] Greaves and Etchells, English Patent, 115866, (April 11, 1917), see *J. Soc. Glass Tech.*, 1919, 3, 194A.

[3] Travers, *J. Soc. Glass. Tech.*, 1921, 5, 166.

[4] Martin, *Industrial Chemistry, Inorganic* (Crosby Lockwood & Son), 1917, Article by Searle, vol. ii, p. 235 ; Rogers, *Industrial Chemistry* (Constable & Co., Ltd.), 1921, Article by Gillinder, p. 336 ; each of these has a bibliography also. Thorpe, *Dictionary of Applied Chemistry* (Longmans, Green & Co.), 1922, vol. iii, p. 378. Numerous papers and abstracts in the *J. Soc. Glass Tech.*

The Properties of Glass.—Ordinary glass is colourless, and transparent to visible light rays, but opaque to ultra-violet and infra-red rays. The density varies from 2·25 for the lightest borate glasses to 6·35 for the heaviest lead and barium glasses. The average for alkali-lime glasses is 2·5–3 0. Glass is a bad conductor of heat, with the result that, when rapidly chilled, the outside cools long before the inside, producing a state of tension, so great in the more extreme cases that any disturbance of the surface, for example by scratching, may cause collapse of the glass to a fine powder with explosive violence. For this reason glass articles, before they are ready for use, must be annealed by heating for some time at a temperature which is fairly high, but not so high that deformation, or devitrification—that is, transformation into a brittle crystalline mass—is produced.[1] The most suitable temperature for annealing varies with composition; for example, if the quantity of silica is kept constant the annealing temperature is reduced as alkali is substituted for lime.[2] If·lime be replaced by magnesium and aluminium, the annealing temperature is in general also lowered.[3] An ordinary soda-lime glass has an annealing temperature in the neighbourhood of 600° C.

The coefficient of cubical expansion varies considerably, the mean value for soda-lime glasses being 0 000023–0 000027.

The change of properties with composition has recently been the object of much more systematic study than formerly. In particular, one might cite the long series of papers by Peddle on the development of various types of glass,[4] and also the work by Turner and his colleagues on soda-lime glasses.[5] Much work, however, still remains to be done. The general results hitherto obtained may be briefly summarised. Apparently contradictory conclusions have sometimes been reached, especially in the earlier work, but these are no doubt due to lack of clear definition of all the conditions.

Alkalies.—Soda and potash make glass more fluid and reduce the rate of setting. They diminish the resistant power towards water and acids, but increase it towards alkalies. Excess of soda especially increases the tendency to devitrification. A mixture of potash and soda produces a more durable glass than either alone.[6]

Lime, substituted for soda up to about 20 per cent., diminishes the tendency to devitrification. It increases the chemical resistance, reduces the heat expansion, and increases the elasticity, rate of setting, and hardness. It makes the glass less fluid at low temperatures, but more fluid at high.

Lead oxide increases the density and refractive index. The glass is readily fusible, but unfortunately blackens when worked in the lamp. Lead glass is extraordinarily resistant to water, but not to acids and alkalies.

Barium oxide, substituted for lime, increases the density and refrac-

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[1] See later.

[2] English and Turner, *J. Soc. Glass Tech.*, 1919, **3**, 125.

[3] Hodkin and Turner, *ibid.*, 1919, **3**, 275; English and Turner, *ibid.*, 1921, **5**, 115.

[4] Peddle, *ibid.*, 1920, **4**, 3, 20, 46, 59, 71, 225, 299, 310, 320, 330; 1921, **5**, 72, 195, 201, 212, 220, 228, 256; *Trans. Opt. Soc.*, 1921–2, **23**, 103, sec *J. Soc. Glass Tech.*, 1922, **6**, 93A.

[5] Turner and others, *ibid.*, 1917, **1**, 153; 1918, **2**, 32, 235; 1919, **3**, 37, 227, 228, 238, 253, 260, 275, 278; 1921, **5**, 107, 119, 183, 277; *J. Soc. Chem. Ind.*, 1918; **37**, 451R. See also work on lime-magnesia glasses, *J. Soc. Glass Tech.*, 1921, **5**, 352, 357; 1922, **6**, 101.

[6] Travers, *ibid.*, 1919, **3**, 253.

tive index, although not to so great an extent as lead ; but it has the advantage over the latter of not blackening in the flame. It also increases the durability and decreases the solubility.

Zinc oxide is useful in glasses for laboratory and optical purposes. It gives a low coefficient of expansion to the glass, but a high tensile strength and chemical resistance.

Magnesia is similar to lime in its effect. It increases the viscosity and the heat-retaining power, which are advantages in working, but there is also a tendency to stringiness. Resistance to acids is slightly increased, but to alkalies it is diminished. Magnesia glass has a lower coefficient of expansion than lime glass, and also a lower annealing temperature.

Thallium oxide is sometimes used for special optical lenses. It makes the glass harder and increases the density and refractive index, but it is expensive.

Aluminium oxide.—The effect of aluminium oxide on glass has been the subject of much controversy in the past, but it now seems generally agreed that, up to a certain limit, the presence of alumina is beneficial. It reduces the tendency to devitrification, the thermal expansion, and the density, and increases the facility of working, although the effect produced depends greatly on the composition of the glass.[1]

Silica gives high viscosity and chemical resistance. In very large quantity it causes devitrification and raises the temperature of fusion. Silica alone may be used as a glass, and has valuable heat-resisting properties ; but a very high temperature, 1700°–1800° C., is necessary for fusion.

Boric acid gives low thermal conductivity and high chemical resistance if not present in too large quantity, for example, not more than 10 per cent., or even less. It was used in old Venetian glass. The coefficient of expansion, tendency to devitrification, and melting-point are lowered, whilst the refractive index is increased. Borosilicate glass is valuable for optical purposes.

Phosphoric acid up to a high percentage may be used in optical glass.

The following formulæ have been given as representing the composition of good all-round glasses [2] :—

Na_2O.	K_2O.	ZnO.	CaO.	MgO.	SiO_2.	B_2O_3.	Al_2O_3.
17·4	0·33	10·3	0 64	Trace	100	9·4	5·6
16·8	2·5	4 0	7 0	0·8	100	5·9	5·9
14·6	1·0	9·7	0·8	0·3	100·	9·0	5·8

Small quantities of selenium,[3] arsenic, and antimony are sometimes introduced to act as decolorisers and to help in fining the glass.

[1] Frink, *Trans. Amer. Ceramic Soc.*, 1909, 11, 99, see *J. Soc. Chem. Ind.*, 1909, 28, 1127 ; Singer, *Keramische Rundschau*, 1915, 5, and 1917, 25, 142 *et seq.*, see *J. Soc. Glass Tech.*, 1917, 1, 16A ; 1918, 2, 53A ; Springer. *Keramische Rundschau*, 1917, 48, 243, see *J. Soc. Glass Tech.*, 1918, 2, 88A ; Turner and colleagues, *loc. cit.*, 1921.
[2] Cauwood, English, and Turner, *J. Soc. Glass Tech.*, 1917, 1, 153.
[3] Cousen and Turner, *ibid.*, 1922, 6, 168 ; Sugie, *Chem. Abs.*, 1922, 16, 4030.

The durability of glass is determined by Mylius' weathering test.[1] The glass is exposed to the action of water for a definite period, and the intensity of the pink colour developed in an ethereal solution of iodo-eosin then noted. Another test, known as the " dimming test," has been suggested.[2] The extent to which moisture is deposited on a carefully cleaned glass plate in an atmosphere of definite moisture content is observed, and the corroding effect afterwards studied under the microscope. A useful bibliography on the durability of glass is given by Turner.[3]

The Constitution of Glass.—A controversial point in the study of glass is the question of its constitution. As glass cools there is no sudden change from fluidity to rigidity as in most cases of solidification, but a gradual decrease in fluidity. The same gradual change is also to be observed in some other properties, for example electrical conductivity,[4] which Ambronn showed to be of an electrolytic nature.[5] This gave rise to the view that glass is a solid solution.[6] Devitrification of glass, which is aided by keeping the glass at softening temperature, thus conferring freedom of movement on the particles, is simply the crystallising out of the various constituents of the solid solution. The continuity of the properties of glass, however, has probably been taken for granted to a greater extent than is justified by experimental evidence.[7] For example, examination of a number of glasses seems to show that at about 70° C. below softening temperature the rate of absorption of heat with rise of temperature undergoes a sudden increase, which is maintained up to a temperature slightly below the softening point. This range coincides with the annealing range within which the glass may be regarded as plastic.[8] The coefficient of expansion remains constant until this plastic region is reached, when a sudden increase to a value four to seven times as great takes place.[9]

According to Zulkowski, the durability of a glass is contingent upon the formation of double silicates, and not of a mixture or solid solution of simple silicates. Deviations from the recognised glass formulæ produce poor glass, because they result in the presence of simple silicates which are more easily attacked.[10] The formation of the double silicates probably takes place in the fining stage.[11]

Another view has been put forward, founded on W. and D. Asch's conception of the structure of the silicic acid molecule.[12] A good glass is to be regarded as a supercooled single chemical compound, with

[1] Mylius, *Zeitsch. anorg. Chem.*, 1907, 55, 233 ; 1910, 67, 200 ; *Silikat-Zeitsch.*, 1913, 1, 2, 25, 45.

[2] Elsden, Roberts, and Jones, *J. Soc. Glass Tech.*, 1919, 3, 52.

[3] Turner, *ibid.*, 1917, 1, 213 ; see also *ibid.*, 1922, 6, 30. See also Rep. of Brit. Sci. Inst. Res. Assoc., 1921, *J. Soc. Glass. Tech.*, 1922, 6, 102A, 167A.

[4] Doelter, *Zeitsch. Elektrochem.*, 1908, 14, 552.

[5] Ambronn, *Physikal. Zeitsch.*, 1913, 14, 112 ; 1918, 19, 401 ; *Ann. Physik.*, 1919, 58, 139.

[6] See *J. Soc. Glass Tech.*, 1919, 3, 12A, from *Sprechsaal*, 1905, 38, 482.

[7] Travers, *The Physics and Chemistry of Colloids*, Publications of Dept. of Sci. and Indust. Research, 1921, p. 62.

[8] Tool and Valasek, *U.S. Bureau Standards, Scientific Papers*, 1920, No. 358.

[9] Peters and Cragoe, *ibid.*, No. 393.

[10] Zulkowski, *J. Soc. Chem. Ind.*, 1899, 18, 760.

[11] Zulkowski, *ibid.*, 1900, 19, 442; see Baillie, *J. Soc. Glass Tech.*, 1922, 6, 68.

[12] W. and D. Asch, *Die Silicate* (Springer, Berlin), 1911, see Vol. V. of this series, Caven, 1917, p. 212 *et seq.*

perhaps small quantities of impurities present. The molecule of the compound is a very large one, typical glass molecules being, for instance, $5Na_2O.7CaO.36SiO_2, 5K_2O.7CaO.36SiO_2, 6K_2O.2PbO.2ZnO.2BaO.36SiO_2$, and $3Na_2O.3K_2O.3PbO.3CaO.36SiO_2$. Substances forming large molecules tend to produce very viscous liquids. It is claimed in support of this theory that, when a glass devitrifies, the crystalline portion has the same composition as the vitreous portion,[1] but this is not always the case. Both calcium silicate, and silica in the form of tridymite, may separate out.[2] Peddle, judging from appearance and optical properties, concluded that the crystals forming in glass were wollastonite,[3] but chemical analysis gave a composition approaching that of the original glass. This, however, he ascribed to occluded glass. In the case of barium glasses a barium silicate, $BaSi_2O_5$, separates out in large crystals, if present to the extent of 57 per cent. or more.[4] The phenomenon of surface devitrification is probably due, at any rate partially, to the volatilisation of alkali from the surface, leaving a glass richer in silica,[5] but recent observations seem to indicate that adsorbed water has an important influence.[6]

Bradford compares the solidification of glass to the setting of a jelly, regarding glass therefore as colloidal.[7] This view would seem to favour a structure similar to that required by the one-compound theory —that is, a silicon-oxygen net-work.[8] It is well known that gelatine, on rapid stirring, becomes more mobile, owing, it is supposed, to the breaking-up of the linked chains of atoms forming the framework of the gel. It would be interesting to know if rapid stirring of glass which has reached a viscous state would make it more fluid again.

Quincke, from a study of the copper aventurine glasses which contain microscopic crystals of copper in a transparent glass developed in lines of similarly orientated octahedra, or distributed over plane or curved surfaces, concluded that glass has a jellylike structure built up of invisible foam walls separating foam cells, the wall and cell content consisting of a series of liquid phases, each containing several modifications of silicic acid.[9]

CALCIUM AND ALUMINIUM.[10]

Calcium Aluminates.—By fusion of calcium oxide or calcium carbonate with aluminium oxide a number of aluminates can be obtained. The chemical individuality of four of these seems to be definitely

[1] Donath and Indra, *Sprechsaal*, 1911, 44, 160, see *J. Soc. Chem Ind.*, 1911, 30, 424.
[2] Le Chatelier, *Compt. rend.*, 1916, 162, 853.
[3] But see Bourgeois, *Ann. Chim. Phys.*, 1883, [5], 29, 433.
[4] Bowen, *J. Amer. Ceramic Soc*, 1919, 2, 261, see *J. Soc. Glass. Tech.*, 1919, 3, 172A.
[5] Brockbank, *Trans. Amer. Ceramic Soc.*, 1913, 15, 600, see *J. Soc. Chem. Ind.*, 1914, 33, 77 ; Cox, *J. Amer. Ceramic Soc.*, 1919, 2, 576, see *J. Soc. Glass Tech.*, 1920, 4, 68A.
[6] Germann, *J. Amer. Chem. Soc.*, 1921, 43, 11 ; see also Jackson, *Chem. News* 1920, 120, 62.
[7] Bradford, *J. Soc. Glass. Tech.*, 1919, 3, 282.
[8] See also Griffiths, *Phil. Trans.*, 1920, [A], 221, 163.
[9] Quincke, *Ann. Physik*, 1915, [4], 46, 1025.
[10] In accordance with the general arrangement adopted in this series this section ought to follow the one on Calcium and Boron, but, on account of the close association of the aluminates with calcium silicates in the study of cement, they are more conveniently considered here.

established, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, and $3CaO.5Al_2O_3$.[1] The possibility of the formation of the compounds, $2CaO.Al_2O_3$, $3CaO.2Al_2O_3$, $6CaO.5Al_2O_3$, and $11CaO.10Al_2O_3$, has also been suggested,[2] but they have not been thoroughly investigated, and it is probable that some or all of them are solid solutions.

Monocalcium Aluminate, $CaO.Al_2O_3$.—By fusing together calcium and aluminium oxides in the electric furnace, Dufau obtained a spinel-like compound in needle-shaped crystals resembling beryllium aluminate or calcium chromite.[3] The melting-point is about $1590°$ C.[4] It sets and hardens with water.

Tricalcium Aluminate, $3CaO.Al_2O_3$.—Campbell regards tricalcium aluminate as a metastable saturated solution of lime in the compound $5CaO.3Al_2O_3$, or as $5CaO.3Al_2O_3$, with 4 molecules of calcium oxide of crystallisation, rather than as a stable compound,[5] but the balance of evidence seems to be in favour of the latter view.

Tricalcium aluminate decomposes with partial fusion at $1535° \pm 2°$ C.,[6] and is therefore best obtained by crystallising from a glass of the same composition a little below this temperature.[7] It does not possess hydraulic properties.

Phillips showed that a colloidal solution of tricalcium aluminate can be obtained, but more readily in lime-water than in pure water.[8] It is a positively charged colloid, not coagulated by heat, but by freezing. It has a high adsorptive power and resembles the sols of ferric, aluminium, and chromic oxides.

A hydrated compound, $3CaO.Al_2O_3.6H_2O$, is obtained as a crystalline precipitate by the action of hot lime-water on potassium aluminate.[9]

$5CaO.3Al_2O_3$ and $3CaO.5Al_2O_3$ both exist in a stable and unstable form.[7] The stable forms have respectively the melting-points $1455° \pm 5°$ C. and $1720° \pm 10°$ C.[10] The unstable forms are only produced under special conditions of cooling of the fused compounds.

By the action of lime-water on metallic aluminium a hydrated crystalline dicalcium aluminate, $Ca_2Al_2O_5.7H_2O$, is obtained.[9]

Calcium aluminates are mainly important from their relation to Portland cement and will be mentioned again under that heading.

Several natural calcium alumino-silicates are known, *anorthite*, $CaAl_2(SiO_4)_2$, *lime garnet*, $Ca_3Al_2(SiO_4)_3$, and several members of the group of minerals known as *zeolites* which have the general formula $M^{..}Al_2Si_nO_2 2n + 4.mH_2O$.[11]

[1] Le Chatelier, *La Silice et les Silicates* (Hermann et Fils), Paris, 1914, p. 548; Rankin and Merwin, *J. Amer. Chem. Soc.*, 1916, **38**, 568; Meissner, *Chem. Zentr.*, 1919, iii, 511.

[2] Martin, *Moniteur Scientifique*, 1915, [v], **5**, 225, see *J. Chem. Soc*, 1916, **110**, Abs. ii, 139.

[3] Dufau, *Compt. rend.*, 1900, **131**, 541.

[4] Le Chatelier, *loc. cit.*; Shepherd, Rankin, and Wright, *Zeitsch. anorg. Chem.*, 1910, **68**, 370; Shepherd and Wright, *Amer. J. Sci.*, 1909, [4], **28**, 293; Rankin and Wright, *ibid.*, 1915, [4], **39**, 1.

[5] Campbell, *J. Ind. Eng. Chem.*, 1917, **9**, 943.

[6] Shepherd and Wright, *loc. cit.*; Bates, *J. Amer. Ceramic Soc.*, 1918, **1**, 679, see *J. Soc. Chem. Ind.*, 1919, **38**, 177A.

[7] Rankin and Wright, *loc. cit.*

[8] Phillips, *J. Amer. Ceramic Soc.*, 1919, **2**, 708, see *J. Chem. Soc.*, 1919, **116**, Abs. ii, 514.

[9] Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 315.

[10] Le Chatelier; Campbell; Shepherd, Rankin, and Wright; Rankin and Wright; *loc. cit.*

[11] Morozewicz, *Bull. Acad. Sci. Cracow*, 1909, 344.

CEMENT.

The early use of lime mortar has already been mentioned. Both the Greeks and the Romans often mixed with the lime and sand certain volcanic deposits really consisting of fused silicates and aluminates. The resulting product was much stronger than ordinary mortar and resisted the action of water, either fresh or salt. It was thus the forerunner of the modern hydraulic cements. The Greeks used Santorin earth and the Romans pozzuolana from Puteoli, near Naples. Failing these, powdered tiles or pottery formed good substitutes. Trass, from the Rhine valley, has similar properties.

Smeaton in England, from 1756 onwards, and Vicat in France, a little later, experimented with hydraulic limes. These were obtained by burning argillaceous limestone. The product, after burning, set hard under water. In 1827 the original patent for Portland cement was taken out by Joseph Aspdin, a bricklayer of Leeds and Wakefield, in Yorkshire. He proposed to grind lime and clay finely with water, and then to dry and calcine until carbon dioxide was entirely expelled. The name was given from a fancied resemblance to Portland stone.

In Aspdin's process the temperature employed was too low to yield the substance now known as Portland cement. This, since the setting up of the first British Standard Specification in 1904, is a carefully standardised product not subject to the variations in quality which characterise the natural, Roman, or rock cement formed by simply calcining siliceous limestone to just below sintering point.

Natural pozzuolanic substances are not cements, but, when mixed with lime, they form hydraulic mortar without further heating. Artificial pozzuolanic substances include various ignited argillaceous materials and certain blast-furnace slags.[1]

Manufacture.[2]—Portland cement is made by burning to clinkering temperature an intimate mixture of calcareous and clayey material of a limited range of composition. It is essential that a finely ground homogeneous mixture should be used. This may be obtained either by a wet or a dry process.

Wet Process.—The raw materials, of which chalk and clay may be taken as typical, are reduced to a creamy " slip " or " slurry " by agitation in a large vat with water. The slurry is roughly screened and passed through a wet tube mill to complete the breaking-up of the coarser particles. Ultimately, the mixture should become so fine that only 2–5 per cent. is retained by a sieve of mesh 5000 per sq. cm. It is finally dried on the floors of drying chambers by waste heat from the kilns, when it shrinks and cracks into blocks of a size convenient for handling and loading into the kilns, or it may be introduced without drying.

[1] For further details on the early history of the cement industry see Desch, *Chemistry and Testing of Cement* (Arnold), 1911.

[2] Desch, *loc. cit.*; Martin, *Industrial Chemistry, Inorganic* (Crosby Lockwood & Son), 1917, vol. ii, Article by Dancaster, p. 77; these two give an extensive bibliography. Blount, *Cement* (Monographs on Industrial Chemistry) (Longmans, Green & Co.), 1920; Munby, *Introduction to the Chemistry and Physics of Building Materials* (Constable & Co., Ltd.), 1909; Meade, *Lime, Cement, and Plaster, Industrial Chemistry*, 1921, p. 304; Dancaster, *Limes and Cements* (Crosby Lockwood & Son), 1916.

Dry Process.—This process, which is more economical in fuel,[1] is now more generally used, especially for hard materials such as limestone, shale, and slag.   These are coarsely crushed and then dried in a rotating cylinder.   They are afterwards mixed in the requisite proportions and very finely ground.   The fine powder is separated from the coarse by sieves or an air-current.   If it is to be burnt in stationary kilns it is moistened and pressed into bricks.

The old-fashioned type of kiln is charged with alternate layers of coke and lumps of dried slurry or pressed bricks.   Combustion is maintained by natural draught, and the process lasts four or five days.   The fuel consumption is high and the temperature variable, but economies may be effected, as in the Dietsch kiln, by using the hot kiln gases for preheating the raw materials, and the hot clinker, as it reaches the bottom of the kiln, to heat the entering air.   Sintering and partial fusion should take place.   It cannot be overburnt.   The clinker is extremely hard and compact, but contains innumerable minute pores and gas cavities.   It is of a dark grey colour with a slight blue or green tint.

Stationary kilns have now been largely replaced by the rotary kiln, which is a cylindrical steel tube, 210 feet long and 8 feet in diameter, increasing to 9 feet near the firing end, and lined with firebricks protected by cement clinker.   It is supported at a slight inclination to the horizontal and is slowly rotated.   The fuel most commonly used is finely powdered bituminous coal, injected into the lower end of the kiln by a current of compressed air.   The slurry of finely powdered material is introduced at the top, and the temperature increases progressively from top to bottom.   There are three stages in the process : first the mixture is dried and organic matter in the clay burnt off ; next the calcium carbonate is decomposed; and, finally, at about 1400°–1500° C., the lime reacts with silica and alumina, producing a sintered mass of clinker.   The process is continuous, the clinker escaping at the lower end. A kiln such as the one described normally produces $7\frac{1}{2}$ tons of clinker per hour with a fuel consumption 28 per cent. of the weight of cement.

The clinker is then very finely ground, often along with a small quantity of gypsum or some other substance, the purpose of which is to delay setting.   A certain amount of steam is frequently admitted into the grinding mill, also with a view to modifying the setting properties by the action of the small fraction of the lime thus set free by hydrolysis.[2]

An inconvenient and even dangerous amount of dust is produced in the grinding, but various mechanical devices have been invented for trapping it, and incidentally the dust thus collected has since proved a useful source of potash.[3]

An average Portland cement has the following percentage composition : SiO_2, 21–23 ; Al_2O_3, 6–9 ; Fe_2O_3, 2–4 ; CaO, 61–63 ; MgO, 1–3 ; SO_3, 1–1·5 ; CO_2+H_2O, 1–2·5 ; and sulphide sulphur, 0–0·1.

[1] Meade, *Concrete* (Mill Sect.), 1921, 18, 135, see *Chem. Abs.*, 1922, 16, 324.

[2] Bamber, *Trans. Concrete Inst.*, 1909, 1, 106, 132.

[3] Jungner, English Patents, 26497, 28970, see *J. Soc. Chem. Ind.*, 1913, 32, 486, 534 ; Treanor, *Met. Chem. Eng.*, 1917, 16, 701 ; Nestell and Anderson, *J. Ind. Eng. Chem.*, 1917, 9, 253, 646 ; Chance, *J. Soc. Chem. Ind.*, 1918, 37, 222T ; Bradley, *Chem. Met. Eng.*, 1918, 19, 457 ; Merz and Ross, *J. Ind Eng. Chem.*, 1919, 11, 39, see *J. Soc. Chem. Ind.*, 1919, 38, 178A ; Extract from U.S. Geol. Survey, *J. Soc. Chem. Ind.*, 1919, 38, 210R.   According to the *Annual Reports on Alkali, etc. Works* for the last few years, for example 1918, 1921, 1922, and 1923, the recovery of potash from cement dust, although under consideration, and carried out to a certain extent, scarcely appears to be a practical proposition.

An increase in the proportion of lime yields a stronger cement until a certain limit is reached above which the cement becomes unsound, cracking or even disintegrating owing to the expansion after setting. Increase in alumina or ferric oxide hastens setting. Ferrites have a lower melting-point than aluminates and so facilitate sintering, as also do alkalies and magnesia.

If free from iron a white cement, used for decorative work, results.

By replacing a large proportion of the alumina by ferric oxide, iron Portland cement, a German cement, is obtained. It is much more satisfactory in marine work than ordinary cement.

Slag cements are made from blast-furnace slag, which is granulated in water and is substituted for clay in the manufacture of Portland cement.[1] If granulated under certain conditions, it may be used as cement without further heating, for example Passow cement, patented in 1901.

Natural cements may be prepared from rock containing lime, silica, and alumina in approximately the correct proportions. They are variable in quality owing to variation in the composition of the rock, and they cannot compete with Portland cement.

Pozzuolanic materials are not cements but burnt clayey materials in which the silica is present in an active form so that, on mixing with lime and then gauging with water, they set like cement.[2]

A mortar made from cement mixed with sand, and usually lime or loam, is employed for structures exposed to the action of running water or waves.

When cement is treated with water, a plastic mass is first formed, and, after becoming friable, finally sets. The hardness then gradually increases until a stony texture is ultimately obtained. The setting of cement is influenced by the presence of foreign substances much in the same way as plaster of Paris.[3]

The Chemical Constitution of Portland Cement, and the mechanism of the setting and hardening process, have afforded subjects for much discussion, and no generally accepted conclusions appear to have been reached as yet. Much has been done by petrographical study of cement clinker. Le Chatelier[4] and Törnebohm[5] introduced the microscopic examination of cement sections. Four different constituents were observed : " Alite," which is apparently the active principle of cement and forms rhombic crystals of composition represented by the formula $3CaO.SiO_2$,[6] with a small quantity of aluminate; " Belite," a finely striated substance, poorer in lime than alite, and sometimes found in a state of partial disintegration, suggesting the presence of unstable dicalcium silicate ; " Celite," a very inert substance, resisting the action of both water and acids, and present in two varieties, white and grey, both probably solid solutions of dicalcium silicate in dicalcium aluminate ; and, finally, " Felite," in the form of rhombic crystals, a constituent not very frequently observed except in blast-furnace slag, and probably the non-hydraulic form of dicalcium silicate.

Later investigators have also recognised the existence of some or all

[1] Steffens, *Stahl und Eisen*, 1900, 20, 1170.
[2] Gallo, *Gazzetta*, 1908, 38, ii, 156.
[3] Rohland, *Ber.*, 1900, 33, 2831 ; *Zeitsch. angew. Chem.*, 1903, 16, 622 ; 1906, 19, 327.
[4] Le Chatelier, *Compt. rend.*, 1883, 96, 1056, and later.
[5] Törnebohm, *Ueber die Petrographie des Portlandzements*, Stockholm, 1897.
[6] See Tricalcium Silicate, p. 126.

of these four constituents, but opinions differ considerably as to their composition.[1]   In the microscopic study of structure some experimenters have utilised the different adsorptive powers of the various constituents for certain dyes.[2]   This gives ground for regarding some portions of the cement clinker as colloidal.

The only finding upon which there seems to be general agreement is, that Portland cement clinker consists of a complex mixture of calcium aluminates and silicates, either as a more or less homogeneous solid solution,[3] or as a heterogeneous mixture of different solid solutions or of single chemical individuals.

The setting of cement is a more complex phenomenon than the setting of plaster.[4]   The reaction with water is very incomplete, because even the most perfectly mixed cement still contains a large proportion of unchanged material after setting and hardening.   Regrinding of set cement gives a product which is still hydraulic.   Hydrolysis of the silicates and aluminates evidently takes place, because crystals of calcium hydroxide are observed in the set cement.   There is no such certainty, however, as to the nature of the resulting silicates and aluminates.

There are, broadly, two theories as to the mechanism of the setting and hardening processes in Portland cement :—

(a) The crystalloid theory which was originally put forward and is still maintained by Le Chatelier.[5]   According to this, the setting of cement is to be explained similarly to the setting of plaster of Paris. The anhydrous cement dissolves to form a solution supersaturated with respect to the hydrated compounds.   These crystallise out in a confused mass of interlocking crystals, thus giving to the product its mechanical strength.

(b) The colloid theory for which Michaelis is responsible.[6]   Michaelis regarded setting as due to the formation of gelatinous hydrated silicates and aluminates, and hardening to the subsequent drying-up of these hydrates forming hard, glue-like masses, impervious to water.   Any slow crystallisation taking place in the midst of this colloidal mass is to be regarded as injurious rather than beneficial.   In set cement only two

[1] Kappen, *Tonind. Zeit.*, 1905, 29, 370. see *J. Soc. Chem. Ind.*, 1905, 24, 498 ; Janecke, *Zeitsch. anorg. Chem.*, 1911, 73, 200 ; 1912, 74, 428 ; 76, 357 ; 1914, 89, 355 ; Szathmary, *Zeitsch. Kryst. Min.*, 1911, 48, 448 ; Shepherd, Rankin, and Wright, *Zeitsch. anorg. Chem.*, 1911, 71, 19 ; Rankin and Wright, *ibid.*, 1912, 75, 63 ; 1915, 92, 213 ; *Amer. J. Sci.*, 1915, [4], 39, 1 ; Kühl, *Tonind. Zeit.*, 1914, 38, 365, see *J. Soc. Chem. Ind.*, 1914, 33, 315 ; Campbell, *Tonind. Zeit.*, 1913, 37, 1907, see *J. Soc. Chem. Ind.*, 1914, 33, 25 ; *J. Ind. Eng. Chem.*, 1914, 6, 706, see *J. Soc. Chem. Ind.*, 1914, 33, 964 ; *J. Ind. Eng. Chem.*, 1917, 9, 943, see *J. Soc. Chem. Ind.*, 1917, 36, 1236 ; Bates, *Trans. Amer. Ceramic Soc.*, 1913, 15, 420, see *J. Soc. Chem. Ind.*, 1914, 33, 81 ; Hattori, *J. Chem. Ind. Tokyo*, 1917, 20, 701 ; 1918, 21, 306, see *J. Soc. Chem. Ind.*, 1918, 37, 59A, 468A ; Hancock, *App. Chem. Reports*, 1920, 5, 222 ; Neumann, *Stahl und Eisen*, 1918, 38, 953.

[2] Rohland, *Zeitsch. anorg. Chem.*, 1907, 56, 46 ; Boudouard, *Compt. rend.*, 1907, 144, 1047 ; Stern, *Zeitsch. anorg. Chem.*, 1909, 63, 160 ; Keisermann, *Koll. Chem. Beihefte*, 1910, 1, 423 ; Blumenthal, *Silikat-Zeitsch.*, 1914, 2, 43, see *J. Soc. Chem. Ind.*, 1914, 33, 964.

[3] Richardson, *Tonind. Zeit.*, 1903, 27, 942 ; Campbell, *J. Amer. Chem. Soc.*, 1904, 26, 1143.

[4] See p. 68.

[5] Le Chatelier, *Ann. Mines*, 1887, [8], 11, 413 ; *J. Soc. Chem. Ind.*, 1888, 7, 847 ; *Trans. Faraday Soc.*, 1919, 14, 8 ; see also Schott, *Chem. Abs.*, 1922, 16, 1493.

[6] Michaelis, *Chem. Zeit.*, 1893, 17, 982 ; *Der Erhärtungsprozess der kalkhaltigen hydraulischen Bindemittel*, Dresden, 1909 ; *Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 9, see *J. Soc. Chem. Ind.*, 1909, 28, 836 ; see also Colony, *School Mines Quart.*, 1914, 36, 1, see *J. Soc. Chem. Ind.*, 1915, 34, 801.

constituents should be observed microscopically : a colloidal medium surrounding particles of unaltered clinker.[1]

Le Chatelier admitted that, in the initial stages, the constituents may be in a colloidal condition. He considered, however, that there is no proof that this persists, even though the particles in the hardened cement may not be recognisable as true crystals, since they are too small to be detected.

Von Glasenapp observed a change in Portland cement after three years. He ascribed this to the slow conversion of colloids into crystalloids.[2]

Desch[3] pointed out that Le Chatelier worked with dilute solutions and Michaelis with concentrated. This, according to Hatschek,[4] would account for the difference between their views, because it is well known that slightly soluble substances may be obtained either as gels, as the familiar crystalline precipitates, or as sols, depending on the concentration of the reacting solutions. It is also possible for the originally formed gel to assume gradually a coarser crystalline structure. In gauging cement a comparatively small quantity of water is used, and, therefore, concentrated solutions are here under consideration.

A considerable amount of work has been done by the United States Geophysical Laboratory and the Bureau of Standards on the constitution, setting, and hardening of Portland cement,[5] and the conclusions may be summarised briefly here. Lime, alumina, and silica are the only essential constituents of good cements. Well-burned clinker contains three compounds capable of independent existence: a-dicalcium silicate,[6] tricalcium silicate, and tricalcium aluminate. If burnt at too low a temperature, or for too short a time, free lime and the compound $5CaO.3Al_2O_3$ are also present. The initial set is probably caused by the hydration of tricalcium aluminate, any free lime being also hydrated to an amorphous product which crystallises later. The hardening, and the development of cohesive strength, are brought about by the slower hydration of tricalcium silicate which forms 30–35 per cent. of the clinker. This process continues for about a month. The dicalcium silicate hydrates still more slowly to a granular porous mass, free lime and gelatinous silica being formed. Subsequent partial crystallisation takes place in the gelatinous hydrated material. Gelatinous silica is probably the chief cementing agent. The value of the aluminate lies, no doubt, in its action as a flux in the burning of the clinker.

Small quantities of foreign salts influence the rate of setting of cement.[7] Rohland regarded the effect as catalytic.[8]

[1] See also Ambronn, *Tonind. Zeit.*, 1909, 33, 270, see *J. Soc. Chem. Ind.*, 1909, 28, 366.

[2] von Glasenapp, *Chem. Zeit.*, 1914, 38, 588 ; see also Rohland, *Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 21.

[3] Desch, *Trans. Faraday Soc.*, 1919, 14, 1.

[4] Hatschek, *ibid.*, 53.

[5] Rankin, *ibid.*, 23 ; Klein, *ibid.*, 14 ; Neumann, *Stahl und Eisen*, 1918, 38, 953. See also Little, this series, Vol. IV., p. 78.

[6] There seems to be some confusion in the naming of the isomorphous dicalcium silicates ; by the a-orthosilicate is here indicated the hydraulic compound which is obtained by rapid cooling from above 1410° C., see p. 126.

[7] Compare Plaster of Paris, p. 68.

[8] Rohland, *Zeitsch. angew. Chem.*, 1903, 16, 622 ; 1906, 19, 327 ; *Zeitsch. Elektrochem.*, 1904, 10, 893 ; Witt, *Philippine J. Sci.*, 1918, 13A, 29, see *J. Soc. Chem. Ind.*, 1918, 37, 336A. But see Jordis, *Zeitsch. Elektrochem.*, 1904, 10, 938.

Fineness of grinding increases the rate of setting and also the tensile strength.

Portland cement should be of a bluish or greenish-grey colour, yellowness indicating insufficient burning.

A satisfactory Portland cement clinker should pass the following tests [1] :—

Fineness.—The ground cement clinker should not leave more than 14 per cent. on a sieve of mesh 180 to the linear inch, and 1 per cent. on one of mesh 76 to the linear inch.

Chemical Composition.—The proportion of lime to silica and alumina, after deduction of the proportion necessary to combine with the sulphuric anhydride present, when calculated (in chemical equivalents) by the formula $\dfrac{CaO}{SiO_2 + Al_2O_3}$, must not be greater than 2·85 nor less than 2·0. The insoluble residue must not exceed 1·5 per cent. ; that of magnesia 3 per cent.; and the total sulphur content, calculated as sulphur trioxide, 2·75 per cent. The total loss on ignition must not exceed 3 per cent.

Setting-time.—Unless an especially quick-setting cement is specified or required it must have an initial setting-time of not less than 20 minutes, and a final setting-time of not more than 10 hours. For a quick-setting cement the initial set should be not less than 2 minutes and the final 30 minutes. The time of initial set is the interval between gauging and partial loss of plasticity, and the time of final set is the time required to attain sufficient firmness to resist a certain definite pressure, usually applied by a loaded Vicat needle. Gary's method of determining the setting-time is to follow the changes of temperature. There is a considerable rise in temperature at the first set and a second rise at the final set.[2]

Tensile Strength.—This is determined by the force required to pull apart a dumb-bell-shaped briquette. It varies with the quantity of water, temperature, and time of setting. Briquettes kept in a damp atmosphere for 24 hours, and in water for 6 days, must have a tensile strength of not less than 400 lbs. per square inch, and, after 28 days, 540 lbs. per square inch.

Soundness.—This test is made by Le Chatelier's method. The apparatus is a split cylindrical mould by which the expansion of the cement after treatment with boiling water can be measured. This expansion must not exceed certain defined limits.

Small quantities of gypsum, up to 2 per cent., may be used with safety as a retarder. In excess of this it produces unsoundness, apparently due to the formation of calcium sulpho-aluminate, $3CaO.Al_2O_3.3CaSO_4.xH_2O$.[3] The destructive action of sea-water on cement and concrete has been ascribed to the formation of this compound,[4] but there seems to be reason to doubt this.[5] The destruction of concrete, however, by surface water, peaty water, sewage, or sulphate

[1] *British Standard Specification for Portland Cement*, 1920.
[2] See also Killig, *Zement*, 1919, 8, 499, 511, 536, 548, see *Chem. Abs.*, 1920, 14, 3515.
[3] Candlot, *J. Soc. Chem. Ind.*, 1891, 10, 140 ; Deval, *Bull. Soc. d'Encour.*, 1901, 101, [1], 96 ; *Tonind. Zeit.*, 1902, 26, 913, 1081 ; *J. Soc. Chem. Ind.*, 1901, 20, 991 ; 1902, 21, 257, 971 ; Klein and Phillips, *J. Wash. Acad. Sci.*, 1914, 4, 573.
[4] Poirson, *Zeitsch. hydr. Zement*, 1910, 1, 151, see *J. Chem. Soc.*, 1911, 100, Abs. ii, 204.
[5] Rebuffat, *Gazzetta*, 1901, 31, 1, 55 ; 1902, 32, ii, 158.

solutions is probably to be attributed to it.[1]   This action may be prevented by the replacement of alumina by iron oxide.[2]

Magnesia is a cause of unsoundness, because it hydrates much more slowly than the other compounds, thus causing changes in volume after the setting of the cement.[3]

Mention has already been made of the unsoundness produced by excess of lime.[4]   According to Erdahl, however, unsoundness is due, not to free lime, but to dicalcium silicate, which disintegrates or "dusts." [5]

The destructive action of sea-water is probably due to the crystallising of alkali salts in the pores,[6] and is best overcome by making impervious to water.[7]

Iron Cement.—When ferric oxide replaces aluminium oxide in cement, calcium ferrites are probably formed.   Percy [8] combined lime and ferric oxide at white heat.   By adding lime-water to a neutral solution of ferric chloride and igniting the resulting precipitate, a compound corresponding to the formula $CaO.Fe_2O_3$ is obtained.[9]   Pelouze obtained $4CaO.Fe_2O_3$ by precipitation.[10]   According to Dufau, however, the pure compound cannot be isolated because it is unstable.[11]

Hilpert and Kohlmeyer,[12] on studying the behaviour of mixtures of calcium and ferric oxides in the electric furnace, concluded that the following compounds existed : calcium orthoferrite, $3CaO.Fe_2O_3$, melting-point 1410° C., disintegrating like calcium orthosilicate on cooling ; $3CaO.2Fe_2O_3$, melting-point 1450° C. ; $5CaO.3Fe_2O_3$, formed by reaction in the solid state at 1220° C. ; $2CaO.3Fe_2O_3$, melting-point 1400° C. ; and probably calcium metaferrite, $CaO.Fe_2O_3$, formed below the eutectic temperature.   They found also that mixtures containing calcium oxide of a molecular percentage of 60–70 are hydraulic.

Cooling curve and micrographic investigations seem to indicate the presence of only mono- and di-calcium ferrite.[13]

From a fused mixture of lime, ferric oxide, and alumina, mixed crystals containing both ferric oxide and alumina crystallise out.   The cooling curves of fused mixtures of silica, lime, and ferric oxide indicate the formation of ferrous silicate and a double compound, $2Fe_2SiO_4.3Ca_2SiO_4$.[14]

More lime can be safely introduced into cements rich in alumina than into those rich in ferric oxide.[15]   Ferric oxide, like alumina, acts as a flux.[16]

[1] Nitzsche, *Zeitsch. angew. Chem.*, 1919, 32, 21.

[2] Michaelis, English Patent, 3768 (1901), see *J. Soc. Chem. Ind.*, 1902, 21, 175.

[3] Glaessner, *J. Soc. Chem. Ind.*, 1902, 21, 1395 ; Campbell, *J. Ind. Eng. Chem.*, 1916, 8, 1101, see *J. Soc. Chem. Ind.*, 1917, 36, 33.

[4] See p. 137.

[5] Erdahl, *Concrete* (Mill Sect.), 1920, 16, 23, see *Chem. Abs.*, 1920, 14, 2403 ; see also Schott, *Chem. Abs.*, 1922, 16, 1494.

[6] Bates, Phillips, and Wig, *J. Franklin Inst.*, 1913, 175, 65, see *J. Soc. Chem. Ind.*, 1913, 32, 196 ; Rebuffat, *loc. cit.*

[7] Gardner, *J. Franklin Inst.*, 1915, 179, 313, see *J. Soc. Chem. Ind.*, 1915, 34, 434.

[8] Percy, *Phil. Mag.*, 1873, [4], 45, 455.

[9] List, *Ber.*, 1878, 11, 1512.

[10] Pelouze, *Ann. Chim. Phys.*, 1851, [3], 33, 5.

[11] Dufau, *ibid.*, 1897, [7], 12, 257.

[12] Hilpert and Kohlmeyer, *Ber.*, 1909, 42, 4581.

[13] Sosman and Merwin, *J. Wash. Acad. Sci.*, 1916, 6, 532 ; Campbell, *J. Ind. Eng. Chem.*, 1919, 11, 116.

[14] Seliwanov, *J. Soc. Chem. Ind.*, 1916, 35, 307.

[15] Campbell, *loc. cit.*

[16] Kühl, *Tonind. Zeit.*, 1914, 38, 537, see *J. Soc. Chem. Ind.*, 1914, 33, 355.

In the hydration of iron Portland cement, tricalcium ferrite and ferrous silicates are formed.[1] According to Ludwig, ferric oxide contributes nothing to the hardening of the cement, and acts only as a flux by forming a fusible glass with alumina, no combination with lime taking place, and probably none with silica.[2]

Concrete.—Concrete structures were well known to the Romans, and those of their buildings which still exist, for example the Pantheon, bear witness to the excellence of their work.

Concrete is obtained by binding together with cement an inert fragmentary material known as the aggregate, and consisting of gravel, limestone, granite, broken bricks, or some other similar material. A graded aggregate is better than a uniform one, and the strength of the concrete depends on the strength of the aggregate and the distance of separation of the particles. Concrete structures may be reinforced by steel rods in such a way that tensile stresses are taken as far as possible by the steel, and compression stresses by the concrete. The chief danger in the use of reinforced concrete, especially for ships, lies in the possibility of the penetration of water or saline solutions to the iron, the consequent rusting causing expansion and breaking up of the concrete.[3] The action has been ascribed to an electrolytic effect.[4]

In the use of concrete tanks discrimination should be exercised as to the liquids introduced into them.[5] Acids, especially those which form soluble calcium salts, must be avoided.[6]

CALCIUM AND TIN.

Calcium Stannate, $CaO.SnO_2$, may be obtained as small, transparent, square plates by fusing together stannic oxide and calcium chloride with a small quantity of calcium oxide at red heat for several hours, cooling, and washing with water and very dilute hydrochloric acid. It is not attacked by acids and very little by fused sodium carbonate.

A hydrated compound, $CaO.SnO_2.5H_2O$, is formed by adding potassium stannate to a solution of calcium chloride and heating to 100° C., when the gelatinous precipitate first separated is converted into small, colourless, transparent crystals, apparently cubical in shape. It is insoluble in water, but dissolves in cold hydrochloric or nitric acid, forming limpid solutions which gelatinise on heating.[7]

Calcium Chlorostannate, $CaSnCl_6.6H_2O$, obtained in very deliquescent, colourless, rhombohedric crystals,[8] is a compound analogous to the chloroplatinates, but less stable.[9]

[1] Blumenthal, *J. Soc. Chem. Ind.*, 1914, 33, 964.

[2] Ludwig, *Tonind. Zeit.*, 1901, 25, 2084, 2112, see *J. Soc. Chem. Ind.*, 1902, 21, 256; see also Zulkowski, *Chem. Ind.*, 1901, 24, 420, see *Chem. Zentr.*, 1901, ii, 564.

[3] Creighton, *Trans. Faraday Soc.*, 1919, 16, 155; Friend, *Trans. Concrete Inst.*, 1917-18, 9.

[4] Rosa, McCollum, and Peters, *Tech. Papers Bur. Stand. Washington*, 1913, No. 18, see *J. Soc. Chem. Ind.*, 1914, 33, 486.

[5] Andrews, *Chem. Age*, 1919, 1, 612.

[6] Heise, *Concrete*, 1920, 17, 169, see *Chem. Abs.*, 1921, 15, 299. There is a general discussion on the Setting of Cements and Plasters, *Trans. Faraday Soc.*, 1919, 14, 1.

[7] Ditte, *Compt. rend.*, 1883, 96, 701.

[8] Topsoé, *Jahresber.*, 1874, 177.

[9] Biron, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 489; see also Lewy, *Ann. Chim. Phys.*, 1846, [3], 16, 306.

A bromostannate, $CaSnBr_6.6H_2O$,[1] and a sulphostannate, $2CaS.SnS_2.14H_2O$,[2] are also known.

Calcium Silicostannate, $CaO.SiO_2.SnO_2$, is prepared by heating silica with stannic oxide and calcium chloride.[3] It forms a bright white crystalline powder similar to sphene.

CALCIUM AND LEAD.

Calcium Orthoplumbate, Ca_2PbO_4, is obtained as a reddish compound by the action of air at red heat on a mixture of lead oxide and calcium carbonate.[4] Kassner suggested the use of this compound for the extraction of oxygen from the air.[5] At 880° C. the dissociation tension is 47 mm., and at 1100° C. 940 mm.[6] It forms a hydrate with 4 molecules of water of crystallisation.

Calcium Metaplumbate, $CaPbO_3.4H_2O$, is formed by heating the orthoplumbate alone or in presence of potash.[7] By heating in air near 250° C., water is lost and a reddish-brown powder formed, probably containing a small quantity of calcium perplumbate, $CaPb_2O_6$.

Kassner suggested that calcium plumbate might be used to oxidise potassium ferrocyanide to ferricyanide, carbon dioxide being passed in to neutralise the potassium hydroxide formed. The residual mixture of calcium and lead carbonates could be retransformed into calcium plumbate by heating in air.[8]

Acid Calcium Plumbate, $CaPbO_3.H_2PbO_3$, or calcium diplumbate, is formed along with lime by heating the metaplumbate with water under pressure.[9] By heating, half the water is driven off at 310° C., probably forming the intermediate compound, calcium tetraplumbate, $Ca_2H_2Pb_4O_{11}$, and the remainder at 380°–400° C.

CALCIUM AND TITANIUM.

Calcium Metatitanate, $CaTiO_3$, is found naturally as the mineral *perowskite*, density 3·97–4·01. It may be obtained artificially by fusing titanium oxide and calcium carbonate with potassium carbonate [10] or calcium chloride.[11] There are probably two modifications of the titanate. At high temperatures it forms homogeneous solid solutions with calcium silicate, but at lower temperatures, when wollastonite is formed, the solutions split up into their components.[12] (See also Calcium Silicotitanate.)

Calcium Fluotitanate, $CaTiF_6.3H_2O$, is obtained by dissolving calcium carbonate in an acid solution of titanium fluoride, and allowing

[1] Preis and Rayman, *Chem. Zentr.*, 1882, 773.
[2] Ditte, *Compt. rend.*, 1882, **95**, 641.
[3] Bourgeois, *ibid.*, 1887, **104**, 231.
[4] Kassner, *Arch. Pharm.*, 1890, **228**, 109.
[5] Kassner, *Chem. Zeit.*, 1898, **22**, 225.
[6] Le Chatelier, *Compt. rend.*, 1893, **117**, 109.
[7] Kassner, *Arch. Pharm.*, 1895, **233**, 507; 1899, **237**, 409; see also Grützner and Höhnel, *ibid.*, 1895, **233**, 512.
[8] Kassner, *Chem. Zeit.*, 1889, **13**, 1701.
[9] Kassner, *Arch. Pharm.*, 1894, **232**, 375.
[10] Ebelmen, *Ann. Chim. Phys.*, 1851, [3], **33**, 34; *Compt. rend.*, 1851, **32**, 710.
[11] Bourgeois, *Compt. rend.*, 1886, **103**, 141.
[12] Smolensky, *Zeitsch. anorg. Chem.*, 1912, **73**, 293.

to crystallise. It is possible that a small quantity of a dihydrate, isomorphous with the corresponding strontium salt, may also be formed.[1] It is partially split up by water.

Calcium Silicotitanate, $CaSiTiO_5$, occurs naturally as the mineral *titanite* or *sphene* in yellow or bluish-green monoclinic crystals of density 3·3–3·7. The synthetic compound, prepared by fusing together calcium oxide, silica, and titanium oxide, forms blue crystals of melting-point 1221° C.[2] When heated to bright redness in carbon dioxide saturated with water vapour at 50° C., calcium titanate is formed.[3]

CALCIUM AND ZIRCONIUM.

Calcium Zirconate, $CaO.ZrO_2$, is prepared by fusing calcium oxide or calcium chloride with zirconia.[4] It forms cubical crystals similar to calcium stannate and titanate.

Calcium Silicozirconate, $CaO.SiO_2.ZrO_2$, isomorphous with calcium silicostannate and sphene, is obtained by fusing calcium oxide with zircon.[5]

CALCIUM AND BORON.

Calcium Boride, CaB_6, may be obtained by heating lime with boron or by reducing calcium borate with aluminium in presence of carbon in the electric furnace,[6] and also by the action of boric acid on calcium carbide.[7] It may be prepared in a purer form by heating calcium with calcium metaborate under pressure and extracting with dilute acetic acid, followed by dilute hydrochloric acid, and finally hot water, when calcium boride is left as a light brown crystalline powder of density 2·11 at 18° C.[8]

Its properties were studied by Moissan. It is hard enough to scratch ruby, and melts at the temperature of the electric arc.

It is attacked by halogens, but not by hydrogen at red heat. It burns when heated to bright redness in air. Below 1000° C. it is not attacked by water, but is slowly decomposed by halogen acids in the gaseous state at red heat. It reduces concentrated sulphuric acid with evolution of sulphur dioxide, and reacts with nitric acid and other oxidising agents.

Calcium Borates.—Calcium borate is found in nature as *boro-calcite*, $CaB_4O_7.4H_2O$, *colemannite*, $Ca_2B_6O_{11}.5H_2O$, and *pandermite*, $Ca_2B_6O_{11}.3H_2O$, the latter being used for the extraction of boric acid. Calcium borates, varying in composition according to the conditions of formation, may be obtained by the action of boric acid on calcium

[1] Marignac, *Ann. Mines*, 1859, [5], 15, 221.

[2] Hautefeuille, *Ann. Chim. Phys.*, 1865, [4], 4, 154 ; Michel, *Compt rend.*, 1892, 115, 830 ; Smolensky, *loc. cit.* ; Bourgeois, *Ann. Chim. Phys.*, 1883, [5], 29, 474.

[3] Hautefeuille, *ibid.*, 1865, [4], 4, 163.

[4] Hjortdahl, *Compt. rend.*, 1865, 61, 213 ; Venable and Clarke, *J. Amer. Chem. Soc.*, 1896, 18, 434.

[5] Ouvrard, *Compt. rend.*, 1891, 113, 80.

[6] Moissan and Williams, *ibid.*, 1897, 125, 629 ; Moissan, *Electric Furnace*, English translation (Williams & Norgate), 1908.

[7] Geelmuyden, *Compt. rend.*, 1900, 130, 1026 ; Stähler and Elbert, *Ber.*, 1913, 46, 2065.

[8] Wedekind, *Ber.*, 1913, 46, 1885 ; see also Muthmann, Weiss, and Metzger, *Annalen*, 1907, 355, 137 ; Stock and Holle, *Ber.*, 1908, 41, 2095.

hydroxide, or by precipitation or fusion of a calcium salt with an alkali borate.[1]

By studying the freezing-point curve of mixtures of calcium oxide and boric anhydride, Guertler confirmed the existence of the compounds, $2CaO.B_2O_3$, melting-point 1225° C.; $CaO.B_2O_3$, melting-point 1095° C.; $CaO.2B_2O_3$, and possibly $3CaO.B_2O_3$, by the position of the maxima on the curve.[2] The flatness of the curves at these points, however, indicate considerable dissociation on fusing.

The heats of formation of the different anhydrous calcium borates are as follows [3] :—

$$2B_2O_3 + \ \ CaO = 2B_2O_3.CaO \ \ +39\ 8\ Cal.$$
$$B_2O_3 + \ \ CaO = B_2O_3.CaO \ \ +30\ 9\ Cal.$$
$$B_2O_3 + 2CaO = B_2O_3.2CaO \ \ +48\ 5\ Cal.$$
$$B_2O_3 + 3CaO = B_2O_3.3CaO \ \ +62\ 2\ Cal.$$
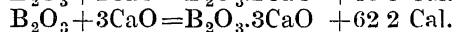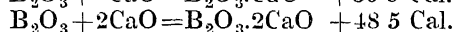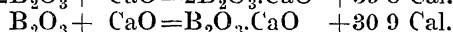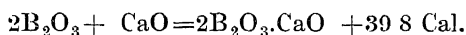
By precipitation, hydrated compounds are formed. Equivalent quantities of calcium hydroxide and boric acid give calcium metaborate hexahydrate, $CaO.B_2O_3.6H_2O$, which is apparently the stable form at ordinary temperatures. According to Meyerhoffer and van 't Hoff, an unstable α-tetrahydrate may exist above 24° C. At 40° C., in contact with a 10 per cent. solution of sodium chloride, this is transformed into the stable β-tetrahydrate.[4] Mandelbaum obtained an amorphous compound, probably a tetrahydrate, by precipitation at 60°–70° C., and this, after a few days, passed into a crystalline hexahydrate, if left in contact with water. The solubility curves of both the tetra- and hexahydrates show decided maxima between 65° and 70° C., and cut at 42° C., evidently the transition point.[5] By heating the hexahydrate to 105° C. two-thirds of the water is driven off, leaving the dihydrate from which the remaining water can only be removed at red heat; for this reason Mandelbaum suggested the formula $CaO\!\!<^{O-B(OH)_2}_{O-B(OH)_2}.4H_2O$ for the hexahydrate.

A tetrahydrate has also been obtained electrolytically.[6]

By the action of boric acid on the metaborate hexahydrate, Meyerhoffer and van 't Hoff obtained the compounds $CaO.3B_2O_3.12H_2O$, $8H_2O$, and $4H_2O$, as well as $2CaO.3B_2O_3.9H_2O$ and $5H_2O$.

A double sodium calcium borate may be prepared and also occurs naturally as the mineral *boronatrocalcite*.[7]

Halogen Compounds of Calcium Borate.—Calcium chloroborates, $3CaO.CaCl_2.5B_2O_3$ and $3CaO.CaCl_2.3B_2O_3$, may be obtained by fusing

[1] Ditte, *Compt. rend.*, 1873, 77, 783 ; 1875, 80, 490 ; *Ann. Chim. Phys.*, 1883, [5], 30, 248 ; Bechi, *J. prakt. Chem.*, 1854, [1], 61, 437 ; 1855, [1], 64, 433 ; Rose, *Annalen*, 1852, 84, 216 ; Laurent, *ibid.*, 1850, 76, 257 ; Popp, *Annalen Suppl.*, 1872, 8, 10 ; Benedikt, *Ber.*, 1874, 7, 703 ; Blount, *Chem. News*, 1886, 54, 208 ; Le Chatelier, *Compt. rend.*, 1891, 113, 1034.

[2] Guertler, *Zeitsch. anorg. Chem.*, 1904, 40, 337 ; see also Ouvrard, *Compt. rend.*, 1901, 132, 257 ; 1905, 141, 351, 1022.

[3] Griveau, *Compt. rend.*, 1918, 166, 993. Griveau writes small cal., but this can scarcely be correct.

[4] Meyerhoffer and van 't Hoff, *Annalen*, 1907, 351, 100; see also van 't Hoff and Behn, *Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 38, 653.

[5] Mandelbaum, *Zeitsch. anorg. Chem.*, 1909, 62, 370.

[6] Levi and Castellani, *Atti R. Accad. Lincei*, 1908, [5], 17, ii, 613.

[7] van 't Hoff, *Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 566.

together boric anhydride and calcium chloride in various proportions with or without lime.[1] Two strictly analogous bromoborates have also been similarly prepared,[2] but no iodine compounds.

Berzelius obtained a gelatinous fluoborate.[3]

Calcium Silicoborate, $2CaO.2SiO_2.B_2O_3.H_2O$, is found naturally as the mineral *datholite*, and can also be prepared artificially by the action of a solution of sodium borate on calcium silicate at high temperatures and pressures.[4]

Calcium Borostannate, $CaO.SnO_2.B_2O_3$, prepared by fusion, is identical with the mineral *nordenskiöldite*.[5]

Calcium Perborate, $CaB_2O_6.xH_2O$, is formed by precipitation from calcium chloride and sodium perborate.[6] It is decomposed by water with the evolution of oxygen.

CALCIUM AND IRON.

Calcium Ferrites have already been described under Iron Cement, p. 141.

Calcium Ferrate, $CaFeO_4$.—If a solution of bleaching powder be heated with a small quantity of ferric chloride, a rose-red solution of calcium ferrate is obtained.[7]

DETECTION AND ESTIMATION OF CALCIUM.

Dry Tests.—Volatile calcium salts give to the non-luminous flame a brick-red colour which may be confused with that due to strontium. The spectroscope, however, affords a means of distinguishing between them, calcium being best characterised by the rays 6220 and 5535 Å.[8] The rays most sensitive photographically are 4226·7, 3968 5, and 3933 7 Å.[9]

When heated on charcoal with sodium carbonate, calcium compounds are changed to the white infusible oxide which is brightly luminescent whilst·hot.

It is stated that as little as 0 002 grm. of calcium carbonate in 1 grm. of the mixed alkaline earth carbonates may be detected by heating 0·5–1 grm. of the mixture in an open porcelain dish with a Teclu burner. extracting with water, and then testing the filtrate with phenolphthalein. A red colour indicates calcium.[10]

Wet Tests.—Riesenfeld and Pfützer found that the spectroscopic method may be made very sensitive by producing an arc between an iridium electrode and a small quantity of solution.   For a concentration of 0·0002 mgm. per c.c. the lines 6162, 4227, and very faintly 5589 Å may be detected.[11]

[1] Le Chatelier, *Compt. rend.*, 1884, **99**, 276 ; Ouvrard, *ibid.*, 1901, **132**, 257 ; 1905, **141**, 351.
[2] Ouvrard, *ibid.*, 1905, **141**, 1022.
[3] Berzelius, *Pogg. Annalen*, 1824, **2**, 124.
[4] de Gramont, *Compt. rend*, 1891, **113**, 83.
[5] Ouvrard, *ibid.*, 1906, **143**, 315.
[6] Melikoff and Pissarjewsky, *Ber.*, 1898, **31**, 678, 953 ; see also Byk, German Patent, 248683 (1910), see *J. Chem. Soc.*, 1912, **102**, Abs. ii, 1171.
[7] Bloxam, *Chem. News*, 1886, **54**, 43 ; Rosell, *J. Amer. Chem. Soc.*, 1895, **17**, 760.
[8] Riesenfeld and Wohlers, *Ber.*, 1906, **39**, 2628.
[9] de Gramont, *Compt. rend.*, 1920, **171**, 1106.
[10] Raikow, *Chem. Zeit.*, 1916, **40**, 781.
[11] Riesenfeld and Pfützer, *Ber.*, 1913, **46**, 3140.

In the ordinary course of analysis the alkaline earths are usually separated as carbonates by the addition of ammonia, ammonium chloride, and ammonium carbonate, to the warm solution containing only calcium, strontium, barium, magnesium, and the alkalies. In the cold the reaction is not very sensitive. No precipitation will take place, for instance, in a cold calcium solution containing less than 25 mgm. per litre. Ammonium chloride, which must be added to prevent the precipitation of the magnesium, also decreases the sensitiveness. A boiling solution of sodium carbonate will produce a precipitate in a solution containing only 1 mgm. of calcium per litre. In this case magnesium also is precipitated and must be separated.[1]

The washed carbonates are then dissolved in acetic acid, and when barium and strontium have been removed by various methods, as chromates, sulphates, sulphites, or iodates,[2] calcium is usually precipitated with ammonium oxalate.[3]

Instead of the oxalate, precipitation as fluoride,[4] or as the double calcium potassium ferrocyanide,[5] has been suggested. Precipitation as ferrocyanide can only be carried out in the presence of strontium and not of barium.[6]

Instead of dissolving the carbonates in acetic acid a different procedure may be adopted. A solution is made in nitric acid and evaporated to dryness on the water bath. The calcium nitrate is extracted by a mixture of equal proportions of alcohol and ether,[7] or by amyl alcohol,[8] the solution evaporated, the residue dissolved in water, and the calcium precipitated as oxalate.

Variations on these two processes appear in most text-books of qualitative analysis.

After removal of silver, mercury, and part of the lead from the original solution by hydrochloric acid, the insoluble sulphates of calcium, strontium, barium, and lead may be precipitated, and the lead sulphate removed by ammonium acetate solution. The remaining sulphates may be either converted to carbonates,[9] or reduced to sulphides by heating with carbon, dissolved in acetic acid, and separated by one of the usual methods.[10] Care must be observed, because the alkaline earth sulphates, especially calcium, have a quite appreciable solubility in ammonium acetate solution.[11] From a mixture of the alkaline earth sulphates, calcium sulphate can be removed by ammonium citrate solution.[12]

[1] Kolthoff, *Pharm. Weekblad*, 1920, 57, 1229.
[2] See Strontium and Barium, Detection.
[3] Reichard, *Chem. Zeit.*, 1903, 27, 1035; Benedict, *J. Amer. Chem. Soc.*, 1906, 28, 1596; Bray, *ibid.*, 1909, 31, 611; Hinds, *ibid.*, 1911, 33, 510; van den Bos, *Chem. Weekblad*, 1913, 10, 665.
[4] Karaoglanow, *Zeitsch. anal Chem.*, 1917, 56, 138.
[5] Caron and Raquet, *Bull. Soc. chim.*, 1906, [3], 35, 1061; Baubigny, *ibid.*, 1895, [3], 13, 326; *Compt. rend.*, 1907, 144, 1342; Gilmour, *Chem. News*, 1915, 111, 217.
[6] Flanders, *J. Amer. Chem. Soc.*, 1906, 28, 1509.
[7] Birnbräuer, *Chem. Zeit.*, 1911, 35, 755; Moser and Machiedo, *ibid.*, 337; Rose, *Pogg. Annalen*, 1860, 110, 292.
[8] Browning, *Amer. J. Sci.*, 1892, [3], 43, 50, 314; *Chem. News*, 1892, 65, 271, 282; 66, 3; *Jahresber.*, 1892, 3532.
[9] Curtman and Frankel, *J. Amer. Chem. Soc.*, 1912, 34, 1493.
[10] Browning and Blumenthal, *Amer. J. Sci.*, 1911, [4], 32, 246.
[11] Marden, *J. Amer. Chem. Soc.*, 1916, 38, 310.
[12] Teodossiu, *Bull. Soc. chim. România*, 1921, 3, 34, see *J. Chem. Soc.*, 1921, 120, Abs. ii, 521.

A colour test has been described for the detection of calcium in the presence of barium and strontium.   If a few crystals of pyrogallol and a few drops of alkali are added to a 2 per cent. solution of the mixture, an intense violet colour indicates calcium, or, if the alkaline earth solution is diluted with half its volume of alcohol, and a few drops of a 1 per cent. gallic acid solution are added, followed by an alkali hydroxide, a rose-red precipitate shows the presence of calcium.   There are also confirmatory colour tests to be applied only in the absence of the other alkaline earths.[1]

For the qualitative microchemical analysis of the alkaline earths, the iodates may be precipitated by iodic acid.[2]   Calcium may also be detected microchemically in the presence of strontium and barium, by evaporation of an acetic acid solution with excess of sulphuric acid.   If the residue be treated with a little water and the solution evaporated after the addition of a small quantity of acetic acid, characteristic crystals of calcium sulphate may be seen under the microscope.[3]

As small a quantity as 0 05 per cent. of calcium may be detected under the microscope, in the presence of strontium, by the precipitation of calcium ammonium arsenate, $Ca(NH_4)AsO_4.7H_2O$.[4]

Gravimetric Estimation of Calcium.—For quantitative determination, calcium is usually precipitated as the oxalate.   The neutral, or slightly ammoniacal solution, which should contain no other metals besides magnesium and alkalies, is treated with ammonium chloride, heated to boiling, and precipitated by the addition of a boiling solution of ammonium oxalate.   On standing, the precipitate becomes coarsely crystalline and settles to the bottom of the beaker.   A little more ammonium oxalate is added to ensure complete precipitation.   The precipitate is washed, first by decantation, and then on the filter with a hot solution of ammonium oxalate.   It is then dried and weighed, after conversion into oxide by strong ignition,[5] or into carbonate by gentle heating with or without ammonium carbonate.[6]   It may also be converted into sulphate by sulphuric acid,[7] or fluoride by hydrofluoric acid,[6] or, finally, it may be estimated as calcium oxalate monohydrate,[8] $CaC_2O_4.H_2O$, by drying four or five hours at 105° C.

When magnesium is present, calcium has a great tendency to occlude magnesium oxalate, the quantity of the latter apparently depending on the concentration of undissociated magnesium oxalate in solution, and on the time of contact with the solution.   Excess of ammonium oxalate should be used, and ammonium chloride,[9] or ammonium chloride and acetic acid,[10] added.   The concentration of magnesium in the solution should not be greater than 1 per cent.[11]

When a proportion of magnesium not greater than 10 parts to 1 of

[1] Schewket, *Biochem. Zeitsch.*, 1913, 54, 285.

[2] Denigès, *Compt. rend.*, 1920, 170, 996 ; see also Bolland, *ibid.*, 1920, 171, 955.

[3] Schoorl, *Zeitsch. anal. Chem.*, 1909, 48, 401.

[4] Sörensen, *Zeitsch. anorg. Chem.*, 1896, 11, 305.

[5] Järvinen, *Zeitsch. anal. Chem.*, 1904, 43, 559 ; Robin, *Compt. rend.*, 1903, 137, 258.

[6] Brunck, *Zeitsch. anal. Chem.*, 1906, 45, 77.

[7] Souchay, *ibid.*, 1871, 10, 323 ; Fresenius, *ibid.*, 326 ; but see Kettle, *Zeitsch. angew. Chem.*, 1904, 17, 685.

[8] Goy, *Chem. Zeit.*, 1913, 37, 1337.

[9] Richards, McCaffrey, and Bisbee, *Zeitsch. anorg. Chem.*, 1901, 28, 71.

[10] Gard, *Proc. Univ. Durham Phil. Soc.*, 1915, 5, 234, see *Chem. Abs.*, 1922, 16, 219.

[11] Canals, *Bull. Soc. chim.*, 1918, [4], 23, 422 ; 1921, [4], 29, 152.

calcium is present, a precipitate free from magnesium is supposed to be obtained by slow precipitation.[1]

Separation of calcium, in the presence of much larger quantities of magnesium than is possible when using ammonium oxalate, may be achieved by the use of aniline and aniline oxalate, or the corresponding quinoline or pyridine mixtures.[2]

When, in spite of all precautions, there is a possibility of the presence of occluded magnesium oxalate, the calcium should be redissolved and reprecipitated.[3]

Calcium may be precipitated in the presence of magnesium as sulphite by the addition of ammonium or sodium bisulphite to the hot solution. It should then be filtered, washed with ammonia, treated with a little ammonium sulphate and sulphuric acid, dried, ignited, and weighed as sulphate.[4]

Precipitation of calcium as sulphate, using alcohol to diminish the solubility, may also be employed. Here again modifications are necessary when magnesium is present in large excess. Good results may then be obtained by repeated precipitation or by the use of lithium sulphate solution in a mixture of 10 per cent. ethyl and 90 per cent. methyl alcohol. The precipitated calcium sulphate may afterwards be redissolved in hydrochloric acid and precipitated as oxalate.[5]

The separation and estimation of calcium as tungstate has also been recommended.[6]

Estimation of calcium in the presence of phosphorus, arsenic, or boron is carried out by precipitation as oxalate with the addition of both acetic acid and ammonium chloride.[7]

Volumetric Estimation.—Calcium may be estimated volumetrically by precipitating the oxalate, washing, dissolving in dilute sulphuric acid, and titrating with potassium permanganate. It is not advisable to have a very large quantity of precipitate since too much washing is required and calcium oxalate is appreciably soluble in pure water.[8] The oxalate may be filtered through a Gooch crucible containing a pad of asbestos previously treated with a warm solution of permanganate and sulphuric acid.[9] Instead of sulphuric acid, hydrochloric may be used for dissolving the oxalate. The titration with permanganate must then be carried out at the ordinary temperature with the addition of manganous sulphate to prevent the evolution of chlorine.[10]

In place of titrating the oxalate in the precipitate, a known amount

[1] Blasdale, *J. Amer. Chem. Soc.*, 1909, **31**, 917; see also Winkler, *Zeitsch. angew. Chem.*, 1918, **31**, 187, 203, 214.

[2] Murmann, *Monatsh.*, 1911, **32**, 105.

[3] Korte, *Trans. Chem. Soc.*, 1905, **87**, 1503.

[4] Carron, *Ann. Chim. anal.*, 1912, **17**, 127.

[5] Kallauner and Preller, *Chem. Zeit.*, 1912, **36**, 449, 462; see also Liesse, *Ann. Chim. anal.*, 1911, **16**, 7; Murmann, *Zeitsch. anal. Chem*, 1910, **49**, 688; Stolberg, *Zeitsch. angew. Chem.*, 1904, **17**, 741; Halla, *Chem. Zeit.*, 1914, **38**, 100; Blomberg, *Chem. Weekblad*, 1914, **11**, 1002.

[6] Saint-Sernin, *Compt. rend.*, 1913, **156**, 1019; but see Smith and Bradbury, *Ber*, 1891, **24**, 2930.

[7] Winkler, *Zeitsch. angew. Chem.*, 1919, **32**, i, 24.

[8] Döring, *ibid.*, 1913, **26**, 478.

[9] Halverson and Schutz, *J. Ind. Eng. Chem.*, 1920, **12**, 77. See also Peters, *Amer. J. Sci.*, 1901, [4], **12**, 216; Bowser, *J. Ind. Eng. Chem.*, 1911, **3**, 82; Fox, *ibid.*, 1913, **5**, 910.

[10] Gooch and Peters, *Zeitsch. anorg. Chem.*, 1899, **21**, 185.

of ammonium oxalate may be used and the excess in the filtrate titrated.[1]

Titration by change in electrical conductivity may also be employed. Calcium alone may be titrated as oxalate, sulphate, or carbonate.[2]

In very dilute solutions calcium may be determined by micro-titration with p-aminophenolazochromotropic acid if nickel is absent.[3]

For special purposes special methods are employed. For example, in the analysis of water the estimation of temporary hardness, which is largely a question of the determination of calcium carbonate and magnesium carbonate in terms of calcium, may be carried out by titrating with decinormal sulphuric acid, using methyl orange as indicator, or preferably methyl red.[4]

Total calcium may be estimated by precipitation with ammonium oxalate and titration of either the precipitate[5] or the residual liquid[6] with permanganate. It may also be determined by adding excess of ammonium carbonate—thus making the calcium carbonate practically insoluble, but dissolving the magnesium carbonate—and then, after filtering the precipitated calcium carbonate, and dissolving in decinormal hydrochloric acid, titrating back with fiftieth-normal baryta solution.[7]

Éwe has given a summary of ten different methods, gravimetric and volumetric, of estimating calcium, and the degree of accuracy to be expected from each.[8]

Electrolytic Estimation.—Methods for the separation and determination of the alkaline earths by electrolysis of a solution of the chlorides have been suggested.[9] A rotating silver anode and a mercury cathode are used.

[1] Döring, *loc. cit.*; Grossfeld, *Chem. Zeit.*, 1917, **41**, 842.

[2] Dutoit, *J. Chim. phys.*, 1910, 8, 12; and with Mojoiu, *ibid.*, 27. See also Duboux, *Chem. Zentr.*, 1910, ii, 1566. See Quantitative Estimation of Barium.

[3] Brenner, *Helv. Chim. Acta*, 1920, 3, 90.

[4] Kay and Newlands, *J. Soc. Chem. Ind.*, 1916, **35**, 445.

[5] Hale, *J. Amer. Chem. Soc.*, 1907, **29**, 1078.

[6] Burgess, *Analyst*, 1907, **32**, 208.

[7] Kay and Newlands, *J. Soc. Chem. Ind.*, 1916, **35**, 447.

[8] Éwe, *Chem. News*, 1920, **121**, 53.

[9] Coehn and Kettembeil, *Zeilsch. anorg. Chem.*, 1904, **38**, 198; Lukens and Smith, *J. Amer. Chem. Soc.*, 1907, **29**, 1455; McCutcheon, *ibid*, 1445; Goldbaum and Smith, *ibid.*, 1909, **31**, 900.

CHAPTER III.

STRONTIUM AND ITS COMPOUNDS.

STRONTIUM.

Symbol, Sr.   Atomic Weight, 87·63 (O=16).

Occurrence.—Strontium is a much rarer element than either calcium or barium.   It is found principally as the sulphate, *celestine*, and along with barium sulphate as *baryto-celestine*, or as the carbonate *strontianite*, isomorphous with aragonite and witherite.   Calcium, strontium, and barium are interchangeable in the mineral *brewsterite*, $H_4[Ba,Sr,Ca]Al_2Si_6O_{18}.3H_2O$.

Strontium is found in minute quantities in many rocks, especially calcareous rocks,[1] in sea water,[2] and in the ashes of sea plants.   It forms 0·02 per cent. of the older part of the earth's crust.[3]   It can replace calcium in egg-shells and bones, and traces have been found in the liver and muscles.[4]

History.—During the latter half of the eighteenth century there was found in the lead mines at Strontian, in Argyllshire, a mineral at first mistaken for witherite, and usually occurring in fibrous or columnar masses.   In 1790 Crawford suggested that it might be a new earth, and this was confirmed by Hope and by Klaproth, 1792–1793, and the name *strontianite* was given.[5]   Strontianite was also mined at Munster and Hamm in Westphalia.   The sulphate *celestine* was first discovered by Clayfield near Bristol, and was so called from the blue colour which it often possesses.[6]   Strontium minerals were first mined in the United States in 1916, but the output has declined since then.[7]

Davy isolated the metal in 1808.[8]

Preparation of Strontium.—The methods adopted for the separation of metallic strontium are similar to those already described under calcium.

[1] Dieulafait, *Ann. Chim. Phys.*, 1878, [5], **15**, 540; 1879, [5], **17**, 387; *Compt. rend*, 1883, **96**, 452; Hillebrand, *J. Amer. Chem. Soc.*, 1894, **16**, 81; Collot, *Compt. rend.*, 1905, **141**, 832.

[2] Dieulafait, *Compt. rend.*, 1877, **84**, 1303.

[3] Clarke, *The Data of Geochemistry, Bull. U.S. Geol. Survey*, 1916, No. 616, p. 34.

[4] Wheeler, *New York Agric. Exper. Stat.*, 1919, Bull. 468, 1, see *Chem. Abs.*, 1920, **14**, 2654; Mendel and Thacher, *Amer. J. Physiol.*, 1904, **11**, 5.

[5] Hope, *Trans. Roy. Soc. Edin.*, 1792, **4**, 3; Klaproth, *Crell's Annalen*, 1793, **2**, 189; 1794, **1**, 99; Pelletier, *Ann. Chim.*, 1797, [1], **21**, 113; Guyton, *ibid.*, 1797, [1], **24**, 216; Kirwan and Higgins, *Crell's Annalen*, 1795, **2**, 119, 205; Fourcroy and Vauquelin, *Ann. Chim.*, 1797, [1], **21**, 276; 1799, [1], **29**, 270.

[6] Thomson, *System of Chemistry*, vol. iii. (Baldwin, Cradock & Joy), 1817, p. 414.

[7] *U.S. Geol. Survey*, Dec. 5, 1920, see *J. Soc. Chem. Ind.*, 1921, **40**, 194R.

[8] Davy, *Phil. Trans.*, 1808, **98**, 333.

Davy electrolysed a mixture of the moistened oxide or chloride with red mercuric oxide, using a mercury cathode, the final product probably being a rich amalgam.[1]   Matthiessen used iron electrodes and an electrolyte of fused strontium chloride mixed with a little ammonium chloride, the temperature being so regulated that the surface remained solid.[2]   By a similar method Borchers and Stockem obtained globules of the metal 10 mm. in diameter.[3]   In more recent times both the submerged cathode [4] and the contact cathode [5] have been successfully used in the electrolysis of a fused mixture of strontium and potassium chlorides (see Calcium).   By employing the contact cathode, sticks of metal, 10 cm. long and 1–2 cm. diameter, have been obtained.[6]

Attempts to prepare the metal by reduction with sodium were even less successful than in the case of calcium, but by using a mixture of sodium with lead, tin, or bismuth, alloys of strontium have been obtained.[7]   Winkler prepared a very impure product by reducing strontium oxide with magnesium.[8]   A very pure metal may be obtained taking strontium amalgam as the starting-point.   The latter may be prepared either by the action of a 20 per cent. sodium amalgam on a saturated solution of strontium chloride at 90° C.,[9] or, preferably, by the electrolysis of a solution of strontium chloride, using a mercury cathode.[10]   Distillation *in vacuo* concentrates the amalgam.   By heating in hydrogen a little below 1000° C. the mercury can be removed and the hydride formed.   Above 1000° C. *in vacuo* the hydride is decomposed and the metal volatilised and condensed to a product of purity 98·6–99 per cent. strontium, which can be increased to 99·4 per cent. by redistillation *in vacuo*.[11]

Reduction of anhydrous strontium oxide by heating with the calculated amount of powdered aluminium for four hours at 1000° C. *in vacuo* also liberates metallic strontium, which condenses to crystals of 99·4 per cent. purity, the yield being 75 per cent. of the theoretical.[12]

Physical Properties.—Strontium is a silvery-white crystalline metal of about the same hardness as lead.   The density, according to Guntz and Galliot,[12] is 2·63.   All the values given by other investigators are somewhat lower, but that is probably due to the presence of impurities.   The specific heat is 0·0742.[13]   The melting-point is about 800° C.,[14] and the metal volatilises at a slightly higher temperature. The specific electrical resistance is $2·48 \times 10^{-5}$ ohm per c.c.[15]   Metallic

[1] See also Hare, *J. prakt. Chem.*, 1840, [1], 19, 249 ; 1841, [1], 22, 383.

[2] Matthiessen, *Annalen*, 1855, 94, 111

[3] Borchers and Stockem, *Zeitsch. Elektrochem.*, 1902, 8, 759.

[4] Trautz, *Verh. Ges. deut. Naturf. Aertze*, 1911, 83, 11, 1, 196, see *J. Chem. Soc.*, 1912, 102, Abs. ii, 349 ; *Zeitsch. Elektrochem.*, 1915, 21, 130.

[5] Neumann and Bergve, *Zeitsch. Elektrochem.*, 1914, 20, 187 ; 1915, 21, 152.

[6] See also Glascock, *J. Amer. Chem. Soc.*, 1910, 32, 1222.

[7] Caron, *Compt. rend.*, 1859, 48, 440 ; 1860, 50, 547.

[8] Winkler, *Ber.*, 1890, 23, 120.

[9] Böttger, *J. prakt. Chem.*, 1834, [1], 1, 303 ; Franz, *ibid.*, 1869, [1], 107, 253.

[10] Guntz and Roederer, *Bull. Soc. chim.*, 1906, [3], 35, 494.

[11] Guntz, *Compt. rend.*, 1901, 133, 1209 ; 1902, 134, 838 ; Guntz and Roederer, *ibid.*, 1906, 142, 400 ; *Bull. Soc. chim.*, 1906, [3], 35, 503 ; Guntz and Bassett, *J. Chim. phys.*, 1906, 10, 1.

[12] Guntz and Galliot, *Compt. rend.*, 1910, 151, 813.

[13] Glascock, *loc. cit.*

[14] Guntz and Roederer, *Compt. rend.*, 1906, 142, 400.

[15] Matthiessen, *Ann. Chim. Phys.*, 1857, [3], 50, 192.

strontium is photoelectrically sensitive, the maximum effect being obtained under green light.[1] The ionic mobility of $\frac{1}{2}Sr^{\cdot}$ is **51**.[2]

The most intense lines in the spectrum of strontium measured in Ångstrom units are the following [3] :—

Arc : Ultra-violet : 2932·0, 3307·6, 3351·3, 3464·6 ; Visible : 4077·9, 4215·7, 4305·6, 4607·5, 4812·0, 4832·2, 4872·7, 4968·1, 5229·5, 5451·1, 5970·4, 6380·9, 6388·5, 6550·5 ; Infra-red : 10038·3, 10916·3, 20262·4.

Spark : Ultra-violet : 2322·4, 3380·9, 3464·6, 3475·0 ; Visible : 3705·9, 4030·5, 4077·9, 4162·0, 4215·7, 4305·6, 4607·5, 6504·3, 6892·9.

Chemical Properties.—Strontium is more electropositive than calcium, but may be less so at higher temperatures.[4] It tarnishes almost immediately on exposure to the air. When finely powdered it ignites spontaneously, producing the oxide and nitride, and it burns in oxygen with a dazzling red flame. It is readily attacked by the halogens, by hydrochloric acid and sulphuretted hydrogen gases, and by phosphorus, arsenic, and sulphur vapours. At a bright red heat it unites with tin and carbon. It readily decomposes water, methyl and ethyl alcohols, and aniline, giving hydrogen, but does not affect dry ether or hydrocarbons. It reacts with carbon dioxide at red heat, forming strontium carbide and oxide.[5] It dissolves in liquid ammonia, and at a sufficiently high temperature it absorbs hydrogen and nitrogen.[6]

Physiological Action of Strontium.—Strontium salts are not as a rule harmful to the human body when pure, but they are often contaminated with barium.[7] In large subcutaneous doses they may slowly cause paralysis.[8] The bromide, iodide, nitrate, and lactate are useful in certain diseases, and strontium will enter the bone in place of calcium, but is not to be regarded as a satisfactory substitute for calcium.[9]

The chloride, bromide, phosphate, nitrate, and acetate are feebly, and the iodide strongly, toxic to vegetation.[10]

Atomic Weight.—*Approximate Atomic Weight.*—The equivalent of strontium in the majority of its compounds is 44. Its properties indicate a position in the Periodic Table in the alkaline earth group, and, therefore, a valency of 2, making the atomic weight about 88. Glascock's value for the specific heat, 0·0742, indicates, according to Dulong and Petit's Law, an approximate atomic weight of 86.

Exact Atomic Weight.—Berzelius, in his atomic weight table for 1814, gave a value for the atomic weight of strontium which, when referred to oxygen as 16, becomes 89·4, and is probably founded on the early analyses of Klaproth. The first recorded determination is that of Stromeyer,[11] who measured the volume of carbon dioxide evolved by strontium carbonate and found an atomic weight of 87·3.

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[1] Case, *Phys. Review*, 1921, [2], 17, 398.

[2] Kohlrausch, *Zeitsch. Elektrochem.*, 1907, 13, 343 (footnote).

[3] Marshall Watts, *Index of Spectra*, Appendix " U " (1911) (Wesley & Son, London; Abel Heywood & Son, Manchester). See also *Tables Annuelles de Constantes et de Données Numériques* (Gauthier-Villars et Cie), 1913–16, vol. iv, pp. 384, 388.

[4] Wilsmore, *Zeitsch. physikal. Chem.*, 1900, 35, 291.

[5] Guntz and Roederer, *Compt. rend.*, 1906, 142, 140.

[6] Guntz and Roederer, *Bull. Soc. chim.*, 1906, [3], 35, 503 ; Glascock, *loc. cit.*

[7] Pelletier, *Ann. Chim.*, 1797, [1], 21, 113 ; Laborde, *J. Chem. Soc.*, 1891, 60, Abs., 99 ; 1892, 62, Abs., 227.

[8] Meltzer and Auer, *Amer. J. Physiol.*, 1908, 21, 449.

[9] Stoeltzner, *Biochem. Zeitsch.*, 1908, 12, 119.

[10] Coupin, *Compt. rend.*, 1900, 130, 791.

[11] Stromeyer, *Schweigger's J.*, 1817, 19, 228.

Other early determinations are summarised in the following table [1] :—

Date.	Investigator.	Number of Experiments.	Ratio Measured.	Atomic Weight.
1826	Rose [2] . .	. .	$SrCl_2 : 2AgCl$ $=100 : 181 \cdot 25$	87·3
1845	Pelouze [3] .	2	$SrCl_2 : 2Ag$ $=73 \ 478 : 100$	87·7
1858	Marignac [4] .	3	$SrCl_2.6H_2O : 2Ag$ $=123 \cdot 442 : 100$	87·33
,,	,,	3	$SrCl_2 : 2Ag$ $=136 \ 268 : 100$	87 44
,,	,,	3	$SrCl_2 : SrSO_4$. $=100 : 115 \ 936$	87·40
1859	Dumas [5] .	3	$SrCl_2 : 2Ag$ $=73 \ 4079 : 100$	87·41
1895	Richards [6] .	8	$SrBr_2 : 2Ag$ $=114 \ 69 \ ? : 100$	87 629
,,	,,	7	$SrBr_2 : 2AgBr$ $=65 \ 883 : 100$	87·620

Richards made fresh determinations in 1905.[7] As the mean of four titrations, he found that the ratio of a certain weight of silver to the weight of strontium chloride required to precipitate it is 100 : 73·477. This gives a value of 87·620.[1]

Finally, in 1910, Thorpe and Francis [8] carried out a number of determinations with salts purified by extensive recrystallisations. Their results are recorded in the table on the following page.

The International Commission on Atomic Weights for 1910 adopted the value

$$Sr = 87 \cdot 63,[9]$$

which is still retained (1925).

Uses.—No use has been made of the metal as such, but its employment in the construction of photoelectric cells has been suggested.[10]

[1] These are not necessarily the values given by the original investigators, but have been recalculated from their experimental data using the values :

$$O = 16 \cdot 000$$
$$Cl = 35 \ 457$$
$$Br = 79 \cdot 916$$
$$Ag = 107 \cdot 880$$
$$S = 32 \cdot 065.$$

[2] See Stromeyer, *Pogg. Annalen*, 1826, 8, 189.
[3] Pelouze, *Compt. rend.*, 1845, 20, 1047.
[4] Marignac, *Annalen*, 1858, 106, 169.
[5] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 191.
[6] Richards, *Zeitsch. anorg. Chem.*, 1895, 8, 253.
[7] Richards, *ibid.*, 1905, 47, 145.
[8] Thorpe and Francis, *Proc. Roy. Soc.*, 1910, [A], 83, 277.
[9] By the anode-ray method for the examination of isotopes, Aston, *Nature*, 1923, 112, 449, finds only one constituent of atomic weight 88, and concludes that the chemical atomic weight at present in use is too low.
[10] Case, *Phys. Review*, 1921, [2], 17, 398.

Number of Determinations.	Ratio Measured.	Atomic Weights. (Recalculated).[1]
6	$SrBr_2 : 2Ag \quad =1\ 1470$	87·644
5	$SrBr_2 : 2AgBr =0\ 65892$	87 652
6	$SrCl_2 : 2Ag \quad =0\ 73490$	87·648
5	$SrCl_2 : 2AgCl =0·55311$	87·648
		Mean $=87·648 \pm 0·0016$
4	$SrCl_2 : SrSO_4 =0\ 863115$	87 672
3	$SrBr_2 : SrSO_4 =1\ 3471$	87·644
		Mean $=87\ 658 \pm 0\ 0107$

Alloys.—By alloying a little strontium with copper for castings, a harder metal is obtained and blow-holes are prevented. The alloy may be prepared either by adding metallic strontium to the melt, or by electrolysing fused strontium chloride, using a copper cathode. The amount of strontium is not sufficient to affect the electrical conductivity.[2] The alloys with lead, tin, and bismuth, obtained by Caron when attempting to prepare metallic strontium, have already been mentioned. An alloy of strontium and zinc, containing 18 per cent. of the former, can be obtained by heating to redness a mixture of 100 grm. of zinc, 50 of sodium, and 200 of strontium iodide.[3] An alloy with cadmium may be similarly obtained, but since cadmium is more volatile than zinc the alloy may be enriched up to about 45 per cent. of strontium by heating *in vacuo*. It takes a fine polish when filed, but quickly tarnishes in contact with air, being apparently not much less reactive than strontium alone. A lead-strontium alloy, of composition Pb_3Sr, and melting at 676° C., has been described.[4]

Strontium amalgamates with mercury, probably with the formation of definite compounds. Davy prepared a strontium amalgam in his efforts to obtain metallic strontium. According to Kerp and Böttger,[5] the only true amalgam has the composition $SrHg_{12}$, and is produced by electrolysing a solution of strontium chloride, using a mercury cathode, at a temperature below 30° C. By draining the product, hard white crystals, probably monoclinic or triclinic in form, are obtained. The compound begins to break up at 60° C., and is completely molten at 70° C. It is quickly oxidised on exposure to air.

[1] These are not necessarily the values given by the original investigators, but have been recalculated from their experimental data using the values:

$$O = 16·000$$
$$Cl = 35·457$$
$$Br = 79·916$$
$$Ag = 107·880$$
$$S = 32·065.$$

[2] *U.S. Geol. Survey*, Dec. 5, 1920, see *J. Soc. Chem. Ind.*, 1921, **40**, 194R.
[3] Gautier, *Compt. rend.*, 1901, **133**, 1005.
[4] Piwowarsky, *Zeitsch. Metallk.*, 1922, **14**, 300, see *J. Chem. Soc.*, 1922, **122**, Abs. ii, 644.
[5] Kerp and Böttger, *Zeitsch. anorg. Chem.*, 1900, **25**, 35.

Other formulæ, however, have been given, for example $SrHg_{11}$, which, on squeezing under 200 kgm. per sq. cm., is said to form $SrHg_{11}$ in cubical crystals.[1] By heating these amalgams under special conditions, silver-white crystalline products are obtained, of hardness 2–3, and of composition corresponding to the formulæ Sr_2Hg_5 and $SrHg_6$. The amalgam $SrHg_{11}$ is apparently unchanged when centrifuged or submitted to a pressure of 5000 kgm. per sq. cm. in an atmosphere of carbon dioxide. The richest amalgam obtainable contains 52 per cent. of strontium. When heated the whole amalgam distils.[2]

An alloy of strontium and iron, containing about 23 per cent. of strontium, may be obtained by heating the two metals together at low redness. The alloy shows a hard, bright, homogeneous surface on filing, but soon tarnishes. It readily decomposes water.[3]

Alloys with lead or tin, for example 5 per cent. of strontium with 95 per cent. of tin, are beginning to find a use commercially as deoxidisers in the purification of metals and alloys.[4]

COMPOUNDS OF STRONTIUM.

General Properties of Compounds of Strontium.—The strontium ion is colourless and divalent. Coloured salts are only obtained with a coloured anion. Strontium salts are used chiefly in pyrotechnics and for medicinal purposes.

STRONTIUM AND HYDROGEN.

Strontium Hydride, SrH_2.—Winkler first obtained the hydride in an impure state by heating equivalent quantities of strontium oxide and magnesium at a low red heat in an atmosphere of hydrogen. A slightly sintered, greyish-brown, readily oxidisable product was formed to which he gave the formula SrH.[5]

Gautier prepared a white compound of composition SrH_2 by heating a 45 per cent. alloy of strontium with cadmium, mixed with 7–8 per cent. of strontium oxide, in a nickel boat in an atmosphere of hydrogen, to incipient red heat. When absorption was complete, the cadmium could be completely volatilised by raising the temperature. By fusion, the hydride was made more compact, and so less easily affected by the atmosphere.[6]

Reference has already been made to the formation of strontium hydride as an intermediate stage in the preparation of metallic strontium by Guntz and Roederer.[7] The absorption of hydrogen by pure strontium begins at about 215° C., and proceeds vigorously at 260° C.[8]

The heat of formation of the hydride from its elements is 38·4 Cal., calculated from the dissociation pressure at different temperatures, or

[1] Kerp, *Zeitsch. anorg. Chem.*, 1898, 17, 305 ; Guntz and Férée, *Bull. Soc. chim.*, 1897, [3], 17, 390.

[2] Guntz and Roederer, *Bull. Soc. chim.*, 1906, [3], 35, 494.

[3] Glascock, *J. Amer. Chem. Soc.*, 1910, 32, 1222.

[4] Vickers, *Metals and Their Alloys* (Crosby Lockwood & Son), 1923, p. 46.

[5] Winkler, *Ber.*, 1891, 24, 1975.

[6] Gautier, *Compt. rend.*, 1901, 133, 1005 ; 1902, 134, 100.

[7] See p. 152.

[8] Dafert and Miklauz, *Monatsh.*, 1913, 34, 1685.

34·7 Cal., calculated from the heat of reaction with water and the heat of formation of strontium hydroxide solution from strontium.[1]

Strontium hydride is a white hygroscopic body of melting-point above 650° C.[2]   It decomposes water very readily, with evolution of hydrogen and considerable rise of temperature.   It reacts with chlorine when the temperature is slightly raised, and with bromine vapour at dull red heat, but not with liquid bromine even on boiling.   It also reacts with the vapours of sulphur and iodine at red heat, and is attacked by nitrogen at about 600° C.[3]   At 70° C., and at a pressure greater than atmospheric, it reacts with sulphur dioxide, giving strontium hydrogen sulphite.[4]   In dry air it is very stable, and burns only slowly at red heat, but it reacts more vigorously in oxygen and with oxidising agents.   It is a powerful reducing agent.[5]

Gautier found that dissociation of strontium hydride begins at about 675° C.,[6] but, according to Ephraim and Michel, dissociation pressure measurements are difficult to carry out accurately, because there is absorption of hydrogen by the metal, or hydride,[7] as well as combination, and also solution of the hydride in the metal.[8]   These investigators found the following dissociation pressures for a product containing 35 per cent. excess of strontium metal :—

Temperature, ° C.	650	692	725	754	779	803	817
Pressure, mm. Hg	200	300	400	500	600	700	760

Strontium hydride is less stable than calcium hydride and more so than the barium compound.[8]

STRONTIUM AND THE HALOGENS.

Strontium Fluoride, SrF_2, is obtained in regular octahedral crystals by fusion of strontium chloride with potassium hydrogen fluoride[9] or with sodium fluoride,[10] or of strontium iodide with manganese fluoride.[11]   It may also be prepared by the precipitation of strontium chloride solution with potassium fluoride, neutralisation of strontium oxide or carbonate by hydrofluoric acid,[12] or by the action of gaseous hydrofluoric acid on strontium chloride at red heat.[9]   The heat of formation of strontium fluoride from its elements is 237·02 Cal.[13]

The density is 4·20–4·24,[14] and the melting-point 1400° C.[15]   On

[1] Guntz, *Compt. rend.*, 1902, **134**, 838.
[2] Dafert and Miklauz, *Monatsh*, 1913, **34**, 1685.
[3] Gautier, *Compt. rend.*, 1902, **134**, 1108.
[4] Moissan, *ibid.*, 1902, **135**, 653.
[5] Gautier, *ibid.*, 1902, **134**, 100.
[6] Gautier, *ibid.*, 1902, **134**, 1108 ; but see Guntz, *ibid.*, 1902, **134**, 838.
[7] Gautier, *loc. cit.*
[8] Ephraim and Michel, *Helv. Chim. Acta*, 1921, **4**, 900.
[9] Poulenc, *Ann. Chim. Phys.*, 1894, [7], **2**, 29.
[10] Roeder, *Dissert.*, Göttingen, 1863.
[11] Defacqz, *Ann. Chim. Phys.*, 1904, [8], **1**, 337.
[12] Berzelius, *Pogg. Annalen*, 1824, **1**, 20.
[13] de Forcrand, *Compt. rend.*, 1911, **152**, 27.
[14] Schröder, *Jahresber.*, 1879, 31.
[15] Winter, *Dissert.*, Leipzig, 1913, see *J. Chem. Soc.*, 1914, **106**, Abs. ii, 126 ; see also Plato, *Zeitsch. physikal. Chem.*, 1907, **58**, 350 ; Poulenc, *loc. cit.*

heating in air at 1000° C. a certain amount of strontium oxide is formed. Hydrochloric acid passed over it at red heat easily decomposes it into strontium chloride and hydrofluoric acid.

The solubility of strontium fluoride in water is only slight, being 117·1 mgm. per litre at 18° C., as determined by conductivity methods.[1] The heat of solution is −2·1 Cal.[2]

Strontium Chloride, $SrCl_2$, was first prepared by Crawford in 1790. It may be obtained by direct combination of its elements, by the action of chlorine[3] or hydrochloric acid on strontium oxide at high temperatures, or by neutralising strontium hydroxide, carbonate, or sulphide with hydrochloric acid solution, evaporating and fusing the residue in a current of hydrochloric acid gas.[4] On a large scale it is prepared by the action of calcium chloride on strontium carbonate.[5] It may be obtained in a gelatinous form by precipitation under suitable conditions.[6]

The heat of formation of strontium chloride from its elements is 195·66 Cal.[7] The melting-point is 874° C.[8] The density is 2·95–3·05[9] at ordinary temperatures, and at the melting-point 2·77.[10] The specific heat is 0·1199.[11] The following values have been found for the specific electrical conductivity of the fused salt[12] :—

Temperature, ° C.	873	900	950	1000	1050	1100
Ohms⁻¹ per c.c.	1·92	1·98	2·14	2·29	2·43	2·56

The decomposition potential of strontium chloride at 880° C. is 3·4 volts,[13] and of the salt dissolved in potassium chloride and calcium fluoride to bring down the temperature of fusion, 3·0 volts at 615° C., whilst the temperature coefficient is $0·715 \times 10^{-3}$.[14]

Strontium chloride is decomposed by superheated steam, giving hydrochloric acid,[15] and when heated in contact with air it loses chlorine, forming the oxide. Bromine partially replaces the chlorine at high temperatures.[16]

Anhydrous strontium chloride is very hygroscopic, but not quite to the same extent as calcium chloride. It dissolves in water with the evolution of 11·14 Cal. of heat per gram-molecule.[2]

[1] Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, 64, 129.
[2] de Forcrand, *loc. cit.*
[3] Weber, *Pogg. Annalen*, 1861, 112, 619.
[4] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 191.
[5] Wackenroder, *Dingl. poly. J.*, 1884, 253, 440 ; 1886, 262, 143.
[6] von Weimarn, *Zeitsch. Chem. Ind. Koll.*, 1908, 3, 89.
[7] de Forcrand, *loc. cit.*
[8] Winter, *loc. cit.* ; Arndt, *Zeitsch. Elektrochem.*, 1906, 12, 337; Plato, *Zeitsch. physikal. Chem.*, 1907, 58, 350. See also Braun, *Pogg. Annalen*, 1875, 154, 190 ; Carnelley, *J. Chem. Soc.*, 1876, 29, 489 ; 1878, 33, 273 ; Le Chatelier, *Bull. Soc. chim.*, 1887, [2], 47, 300 ; Meyer, Riddle, and Lamb, *Ber.*, 1894, 27, 3129 : McCrae, *Wied. Annalen*, 1895, 55, 95.
[9] Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415; Schiff, *Annalen*, 1858, 108, 23 ; Schröder, *Jahresber.*, 1879, 31 ; Winter, *loc. cit.*
[10] Quincke, *Pogg. Annalen*, 1869, 138, 141.
[11] Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 129.
[12] Arndt, *loc. cit.*
[13] Arndt and Willner, *Zeitsch. Elektrochem.*, 1908, 14, 216.
[14] Neumann and Bergve, *ibid.*, 1915, 21, 152.
[15] Kraus, *Pogg. Annalen*, 1838, 43, 138.
[16] Potilitzin, *Ber.*, 1874, 7, 733 ; 1875, 8, 766.

The following values have been found for the solubilities at different temperatures [1] :—

Temperature, ° C.	−17°	−11°	−5°	−1°	2°	7°	18°	35°	55°	64°
Grams $SrCl_2$ per 100 grams solution	26 5	28·6	29 3	30 8	31 3	31·7	33 7	37 8	43 8	46·4
	75°	98°	105°	118°	132°	153°	175°	215°	250°	
	46 5	49 6	50·7	52 0	52·5	55 7	60 5	64 1	67·3	

There seems to have been some doubt as to the nature of the solid phase in the neighbourhood of 75° C., so that probably equilibrium was not reached.

Harkins found that hydrochloric acid diminished the solubility of strontium chloride from 5160 milli-equivalents per litre at 0° to 425 milli-equivalents in a solution containing 5275 milli-equivalents of hydrochloric acid per litre.[2]

The solubility in alcohol is not very great.[3]

The boiling-points of concentrated aqueous solutions have been studied by Gerlach.[4] A solution containing 487·5 grm. of the anhydrous chloride in 100 grm. of water has a boiling-point of 117° C. Freezing-point determinations of both dilute [5] and concentrated [6] solutions have been made. Aqueous solutions have also been studied from the point of view of surface tension,[7] compressibility,[8] viscosity,[9] electrical conductivity,[10] density,[11] and vapour pressure.[12] The equilibria between strontium and potassium amalgams of different concentrations and solutions of strontium and potassium chlorides have been investigated.[13]

The Hydrates of Strontium Chloride.—Vapour pressure measurements indicate only a hexa- and a di-hydrate,[14] although Etard [15] suggested the possibility of a mono-hydrate.

Strontium Chloride Hexahydrate, $SrCl_2.6H_2O$, crystallises from solutions at ordinary temperatures.[16] It forms colourless hexagonal needles

[1] Etard, *Ann. Chim. Phys.*, 1894, [7], 2, 533.

[2] Harkins *J. Amer. Chem. Soc*, 1911, 33, 1851; see also Engel, *Ann. Chim. Phys.*, 1888, [6], 13, 376; Ditte, *ibid.*, 1881, [5], 22, 559.

[3] Gérardin, *ibid.*, 1865, [4], 5, 156; Fresenius, *Annalen*, 1846, 59, 127.

[4] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 442, 502; see also Kremers, *Pogg. Annalen*, 1854, 92, 497; Legrand, *Ann. Chim. Phys.*, 1835, [2], 59, 436.

[5] Arrhenius, *Zeitsch. physikal. Chem.*, 1888, 2, 491; Loomis, *Wied. Annalen*, 1897, 60, 523; Jones and Chambers, *Amer. Chem. J.*, 1900, 23, 94; Biltz, *Zeitsch. physikal. Chem.*, 1902, 40, 185; Jones and Getman, *ibid*, 1903, 46, 244.

[6] Rüdorff, *Pogg. Annalen*, 1872, 145, 599; de Coppet, *Ann. Chim. Phys.*, 1872, [4], 25, 524; 26, 110.

[7] Timberg, *Wied. Annalen*, 1887, 30, 545.

[8] Schumann, *ibid.*, 1887, 31, 14.

[9] Wagner, *Zeitsch. physikal. Chem.*, 1890, 5, 31.

[10] Kohlrausch and Holborn, *Leitvermögen der Elektrolyte* (B. G. Teubner, Leipzig), 1898; MacGregory, *Wied. Annalen*, 1894, 51, 126 Jones and Chambers, *Amer. Chem. J.*, 1900, 23, 89; Jones and Getman, *Zeitsch. physikal. Chem.*, 1903, 46, 266.

[11] Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 252, 283; Kohlrausch, *Wied. Annalen*, 1879, 6, 38.

[12] Tammann, *Wied. Annalen*, 1885, 24, 549; *Zeitsch. physikal. Chem.*, 1888, 2, Ref., 45; Biltz, *ibid.*, 1902, 40, 185.

[13] Smith and Rees, *J. Amer. Chem. Soc.*, 1918, 40, 1802.

[14] Baxter and Lansing, *ibid.*, 1920, 42, 419; Andreae, *Zeitsch. physikal. Chem.*, 1891, 7, 248; Frowein, *ibid.*, 1887, 1, 5; Lescœur, *Compt. rend.*, 1886, 103, 1260.

[15] Etard, *Ann. Chim. Phys.*, 1894, [7], 2. 533; see also Pareau, *Wied. Annalen*, 1877, 1, 53, 61.

[16] Etard, *Compt. rend.*, 1891, 113, 854.

isomorphous with calcium chloride hexahydrate.[1] The density is 1·954.[2] The heat of formation of the hexahydrate from the anhydrous salt and water is 18·64 Cal., and the heat of solution is −7·50 Cal.[3] The vapour pressure at 25° C. is 8·37 mm.[4]

The hexahydrate is very soluble in methyl alcohol, much more so than in ethyl alcohol.[5]

The temperature of transition to the dihydrate has been carefully determined by Richards and Yngve as 61·34° C.[6] It is lowered by contact of the salt with a solution containing hydrochloric acid; at 25° C. the two hydrates are in equilibrium with a solution containing 2·11 per cent. of strontium chloride and 27·14 per cent. of acid.[7]

Strontium Chloride Dihydrate, $SrCl_2.2H_2O$, crystallises from solutions above the transition point in slightly deliquescent prisms. It may be obtained at ordinary temperatures from a solution of strontium chloride in concentrated hydrochloric acid,[8] or by passing hydrochloric acid gas into a saturated solution of strontium chloride. The heat of hydration of anhydrous strontium chloride to the dihydrate is 9·06 Cal.[9]

There appears to be no record of the temperature of transition from the dihydrate to the anhydrous form, but it is not below 130° C.[10]

Addition Compounds.—Anhydrous strontium chloride absorbs dry ammonia, forming a voluminous white powder of approximate composition, $SrCl_2.8NH_3$. The dissociation pressure is 100 mm. at 3·5° C. There is also a monammoniate, $SrCl_2.NH_3$, which has a vapour pressure of 100 mm. at 45·5° C. The heat of formation of the octammoniate is 9·98 Cal., and of the monammoniate 10·5 Cal. at 0° C., 12·5 at 78° C., and 13·4 at 108° C.[11] Addition compounds are also formed with hydroxylamine, $2SrCl_2.5NH_2OH.2H_2O$ and $2SrCl_2.9NH_2OH.3HCl.H_2O$,[12] and one with glycine, $SrCl_2.2NH_2CH_2COOH.3H_2O$.[13]

Double Salts.—On the following page is a list of the double salts formed by strontium chloride.

It has been suggested that double salts in solution may contain the ion $SrCl_4^{--}$.[14]

Strontium chloride forms mixed crystals or solid solutions, but not compounds with calcium chloride,[15] barium chloride,[16] and lead chloride.[17]

[1] Marignac, *Ann. Mines*, 1856, [5], 9, 3.
[2] Schröder, *Jahresber.*, 1879, 31; Clarke gives 1·964 at 16 7° C, *Amer. Chem. J.*, 1883, 5, 240.
[3] Thomsen, *Thermochemistry*, English translation by Burke (Longmans, Green & Co.), 1908, pp. 62, 64. For the heat of hydration per gram-molecule of water Frowein (*loc. cit.*) found 3·190 Cal.=19·14 Cal. for the total heat.
[4] Baxter and Lansing, *loc. cit.*; Schumb found 8·52 mm., *J. Amer. Chem. Soc.*, 1923, 45, 342.
[5] Lobry de Bruyn, *Zeitsch. physikal. Chem.*, 1892, 10, 787.
[6] Richards and Yngve, *J. Amer. Chem Soc.*, 1918, 40, 89; see also Etard, *loc. cit.*
[7] Milkan, *Zeitsch. physikal Chem.*, 1918, 92, 503.
[8] Ditte, *Ann. Chim. Phys.*, 1881, [5], 22, 559.
[9] Thomsen, *loc. cit.*
[10] Etard, *loc. cit.*
[11] Hüttig, *Zeitsch. anorg. Chem.*, 1922, 124, 322; see also Rose, *Ann. Chim. Phys.*, 1836, [2], 62, 316.
[12] Antonow, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 476.
[13] Pfeiffer and von Modelski, *Zeitsch. physiol. Chem.*, 1912, 81, 329.
[14] Noyes and Falk, *J. Amer. Chem. Soc.*, 1911, 33, 1455.
[15] Sandonnini, *Atti R. Accad. Lincei*, 1911, [5], 20, ii, 496; Schaefer, *Jahrb. Min.*, 1914, i, 15.
[16] Vortisch, *Jahrb. Min. Beil. Bd.*, 1914, 38, 185.
[17] Sandonnini, *Atti R. Accad. Lincei*, 1911, [5], 20, ii, 646.

Salt	Remarks.	Authority.
2KCl SrCl$_2$ . . . KCl.2SrCl$_2$ . . .	M -pt., 597° C. $\Big\}$ both M.-pt., 638° C. $\Big/$ form mixed crystals with BaCl$_2$	Vortisch, *Jahrb. Min. Beil. Bd.*, 1914, **38**, 185.
2NaCl.SrCl$_2$ . . .	..	Berthelot and Ilosvay, *Ann. Chim. Phys.*, 1885, [5], **29**, 318.
5CsCl.2SrCl$_2$.8H$_2$O .	..	Jamieson, *Amer. J. Sci.*, 1917, [4], **43**, 67.
SrCl$_2$.ZnCl$_2$ . . .	Formed at 476° C. Decomp. on melt- ing.	Sandonnini, *Atti R. Accad. Lincei*, 1912, [5], **21**, ii, 524.
SrCl$_2$.ZnCl$_2$.4H$_2$O .	..	Ephraim and Model, *Zeitsch. anorg. Chem.*, 1910, **67**, 379.
SrCl$_2$.2HgCl$_2$.2H$_2$O .	Prismatic crystals very soluble in water.	Bonsdorff, *Pogg. Annalen*, 1829, **17**, 122; but see Harth, *Zeitsch. anorg. Chem.*, 1897, **14**, 323.
SrCl$_2$ 3HgCl$_2$.xH$_2$O .	..	Swan, *Amer. Chem. J.*, 1898, **20**, 632.
SrCl$_2$ 2Hg(CN)$_2$.6H$_2$O .	..	Varet, *Compt. rend.*, 1895, **121**, 348
SrCl$_2$ HgO 6H$_2$O . .	White slender needles decomp. by water.	André, *Compt. rend.*, 1887, **104**, 431.
SrCl$_2$.2TlCl$_3$.6H$_2$O .	..	Gewecke, *Annalen*, 1909, **366**, 223.
SrCl$_2$ SnCl$_4$.8H$_2$O .	..	Topsoe, *Jahresber.*, 1874, 180.
SrCl$_2$.2PbO.5H$_2$O .	Formed by boiling PbO with SrCl$_2$ solution.	André, *Compt. rend.*, 1887, **104**, 359.

Strontium Perchloride.—At low temperatures chlorine is apparently more soluble in strontium chloride solution than in pure water, and on cooling no chlorine hydrate separates out.[1] This may possibly be due to the formation of a perchloride in solution.[2]

Strontium Bromide, SrBr$_2$, may be obtained by dissolving the oxide, carbonate, or sulphide in hydrobromic acid, evaporating to dryness, and heating the residue in a current of the gaseous acid.[3] A gelatinous strontium bromide has also been obtained.[4]

The heat of formation of strontium bromide from its elements is 176·5 Cal.[5]

It is a colourless salt, melting without decomposition at 643° C.,[6] and volatilising at 770° C.[7] It can be heated to dryness in a platinum dish over a free flame without the slightest loss of halogen.[8]

The salt dried at 200° C. has a density of 4·216 at 24° C.[8]

The fused salt is less hygroscopic than the powdered.[8]

Strontium bromide is readily soluble in water, the heat of solution

[1] Goodwin, *Ber.*, 1882, **15**, 3039.
[2] See Calcium Perchloride.
[3] Berthemot, *J. Pharm. Chim.*, 1830, [2], **16**, 660.
[4] See Strontium Chloride.
[5] de Forcrand, *Compt. rend.*, 1911, **152**, 27.
[6] Kellner, *Zeitsch. anorg. Chem.*, 1917, **99**, 137; see also Carnelley, *Trans. Chem. Soc.*, 1878, **33**, 273.
[7] Stock and Heynemann, *Ber.*, 1909, **42**, 4088.
[8] Richards, *Zeitsch. anorg. Chem.*, 1895, **8**, 253.

being 16·1 Cal.[1] The following values have been obtained for the solubilities at different temperatures :—

Temp., °C.	Concentration of $SrBr_2$ in Grams per 100 Grams Solution.		Solid Phase in contact with Solution.	Authority
— 1 7	6·9		Ice	Milikan, *Zeitsch. physikal. Chem.*, 1918 (1916), **92**, 75.
— 4·2	13·9			
— 8·4	23·2			
— 13·5	29 8			
— 19 0	34 8			
— 28·0	41 7		Ice and $SrBr_2.6H_2O$ } eutectic	
	(1)	(2)		(1) Etard, *Ann. Chim. Phys.*, 1894, (7), **2**, 540. (2) Kremers, *Pogg. Annalen*, 1858, **103**, 66.
— 11	43·1		$SrBr_2.6H_2O$	
— 1	47·0			
+ 0		46·8		
7	48·2			
20	51·8	50·0		
40		53·1		
60		57·4		
80		63·6		
93	68·7		$SrBr_2.xH_2O$	
107	69·8			
110		71·4		

Densities of strontium bromide solutions,[2] vapour pressures,[3] freezing-points, electrical conductivities,[4] and refractive indices,[5] have been determined.

The Hydrates of Strontium Bromide.—The existence of two hydrates, the hexa- and the mono-hydrate, has been definitely established,[6] but there is probably also a dihydrate,[7] and Thomsen considered that calorimetric determinations indicated the existence of four hydrates, with 1, 2, 5, and 6 molecules of water of crystallisation respectively.[8]

Strontium Bromide Hexahydrate, $SrBr_2.6H_2O$.—The experiments of Rammelsberg first indicated the existence of this hydrate isomorphous with the chloride hexahydrate.[9] It is hygroscopic, and melts at 100° C. in its own water of crystallisation.[10] The vapour pressure of the salt

[1] de Forcrand, *loc. cit.*
[2] Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 285 ; Jones and Getman, *Zeitsch. physikal. Chem.*, 1904, 49, 405.
[3] Tammann, *Wied. Annalen*, 1885, 24, 552; *Zeitsch. physikal. Chem.*, 1888, 2, Ref., 45.
[4] Jones and Chambers, *Amer. Chem. J.*, 1900, 23, 89 ; Jones and Getman, *loc. cit*
[5] Jones and Getman, *loc. cit.*
[6] Lescoeur, *Ann. Chim. Phys.*, 1890, [6], 19, 553 ; Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 929.
[7] Richards and Yngve, *J. Amer. Chem. Soc.*, 1918, 40, 89.
[8] Thomsen, *J. prakt. Chem.*, 1878, [2], 18, 44.
[9] Rammelsberg, *Pogg. Annalen*, 1842, 55, 237.
[10] Richards, *loc. cit.*

at 20° C. is 1·8 mm.[1]   The heat of hydration is 23·33 Cal.,[2] and the heat of solution of the hydrate −7·22 Cal.   The density is 2·358.[3]

Strontium Bromide Dihydrate, $SrBr_2.2H_2O$.—According to Richards and Yngve, transition from the hexahydrate to the dihydrate takes place at 88·62° C.   The heat of hydration to the dihydrate is 9·95 Cal.,[2] and the heat of solution 6·16 Cal.[2]

Strontium Bromide Monohydrate, $SrBr_2.H_2O$.—The hexahydrate loses 5 molecules of water in the desiccator, or at 100° C. in air, giving the monohydrate.[4]   The heat of hydration is 6·15 Cal., and the heat of solution 9·96 Cal.[2]

Addition Compounds.—With ammonia strontium bromide forms the compound $SrBr_2.8NH_3$, $SrBr_2.2NH_3$, and $SrBr_2.NH_3$, which have a dissociation pressure of 100 mm. at the temperatures 30°, 68°, and 146° C. respectively, and the heats of formation 10·9, 12·8, and 16·2 Cal.[5] There is also evidence of the existence of a labile isomeride of the diammoniate with a pressure of 143 mm. at 63° C.[6]   The anhydrous salt is soluble in ethyl alcohol, and from the solution the compound $2SrBr_2.5C_2H_5OH$ crystallises out in large orthorhombic prisms.[7]   An addition compound with glycine, $SrBr_2.2NH_2CH_2COOH.3H_2O$, has also been obtained.[8]

Double Salts.—Strontium bromide forms double salts with mercuric bromide, $2HgBr_2.SrBr_2$,[9] and $SrBr_2.HgBr_2$, and with mercuric cyanide, $2Hg(CN)_2.SrBr_2.6H_2O$.[10]   Freezing-point curves of mixtures of strontium bromide with bromides of the alkali metals, indicate the existence of the compounds $2SrBr_2.LiBr$, $SrBr_2.2KBr$, and $2SrBr_2.KBr$.[11]

Strontium Perbromide.—Determinations of freezing-point lowering in aqueous solutions of strontium bromide and bromine indicate the presence of a tetrabromide in solution, but if formed at all in the solid state it is a very unstable compound.[12]

Strontium Iodide, SrI_2, is formed when metallic strontium is heated in iodine vapour.[13]   It may be prepared by the action of hydriodic acid, or iodine, and a reducing agent, on strontium hydroxide, carbonate, or sulphide, evaporation, and fusion of the residue in a current of gaseous hydriodic acid.[14]

The heat of formation from its elements is 147·5 Cal.[15]

It is a white deliquescent compound of density 4·549 at 25° C.,[16] and melting-point 507° C., or probably higher, since most of Carnelley's

[1] Lescœur, *loc. cit.*

[2] Thomsen, *Thermochemistry*, English translation by Burke (Longmans, Green & Co.), 1908, p. 64.

[3] Favre and Valson, *Compt. rend.*, 1873, **77**, 579.

[4] Richards, *loc. cit.*

[5] Huttig, *Zeitsch. anorg. Chem.*, 1922, **124**, 322 ; see also Rammelsberg, *Pogg. Annalen*, 1842, **55**, 238, who described a compound, $2SrBr_2.NH_3$.

[6] Huttig, *loc. cit*

[7] Fonzes-Diacon, *J. Pharm. Chim.*, 1895, [6], **1**, 59

[8] Pfeiffer and von Modelski, *Zeitsch. physiol Chem.*, 1912, **81**, 329.

[9] Löwig, *Jahresber.*, 1833, 136.

[10] Varet, *Compt. rend.*, 1895, **121**, 398

[11] Kellner, *Zeitsch. anorg. Chem.*, 1917, **99**, 137.

[12] Meyer, *ibid*, 1902, **30**, 121.

[13] Matthiessen, *Annalen*, 1855, **94**, 110.

[14] See also Calcium Iodide.

[15] de Forcrand, *Compt. rend.*, 1911, **152**, 27 ; see also Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 115.

[16] Baxter and Brink, *J. Amer. Chem. Soc.*, 1908, **30**, 46.

results are rather low.[1] It readily loses iodine if melted in contact with air,[2] and in moist air at ordinary temperatures it is decomposed, forming iodine and strontium hydroxide.

Strontium iodide is even more soluble in water than either the bromide or the chloride.[3] The heat of solution is 20·5 Cal.[4]

Etard found the following values for the solubility [5] :—

Temperature, °C.	−20	−10	−3	+7	+11	+18	38
Grams SrI_2 in 100 grams solution	60·0	60·3	62·2	63 0	63·4	63·5	64 8
	52	77	81	97	105	120	175
	66·0	70·5	74·0	79·2	79·4	80 8	85·6

Measurements of the densities of strontium iodide solutions have been made,[6] and also of refractive indices and freezing-points,[7] and of electrical conductivities.[8] Electrical conductivity determinations of solutions in methyl, ethyl, and propyl alcohol, and in mixtures of these with water, have been made at 0° C. and 25° C.[9]

Hydrates of Strontium Iodide.—From solutions at ordinary temperatures, hexagonal crystalline plates of the hexahydrate separate out.[10] According to Tassilly, the salt obtained at 60° C. contains 7 molecules of water,[11] and the heat of solution is −4·47 Cal. The heat of hydration is, therefore, 25·24 Cal.

Etard separated a duodecahydrate at low temperatures, and concluded that a dihydrate, which may be isomorphous with barium chloride dihydrate, $BaCl_2.2H_2O$, is probably the stable form above 90° C.[5]

Addition Compounds.—Strontium iodide forms addition compounds containing 1, 2, 4, and 6 molecules of ammonia. The compound, $Sr(NH_3)_6I_2$, has a dissociation pressure of 50 mm. at 62° C., and the heat of formation from strontium iodide and ammonia at the same temperature is 13·40 Cal.[12] Hüttig has found compounds with 1, 2, 6, and 8 molecules of ammonia which attain a dissociation pressure of 100 mm. at 204°, 134°, 74·5°, and 31° C. respectively, the heats of formation being 11·0, 12·6, 15·5, and 18·3 Cal.[13]

Double Salts.—The following double salts have been described (see next page).

Strontium Periodides.—By exposure to light of the mother liquor of the double strontium lead iodide, golden-brown crystals of strontium tri-iodide, $SrI_3.15H_2O$, are obtained.[14]

Solid periodides can be obtained by fusing together iodine and strontium iodide in the proper proportions on the water-bath.[15]

[1] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.
[2] Berthelot, *Ann. Chim. Phys.*, 1878, [5], 15, 191 ; Schultze, *J. prakt. Chem.*, 1880, [2], 21, 419.
[3] Kremers, *Pogg. Annalen*, 1858, 103, 57.
[4] de Forcrand, *Compt. rend.*, 1911, 152, 27 ; see also Tassilly, *Ann. Chim. Phys.*, 1899, [7], 17, 115.
[5] Etard, *ibid.*, 1894, [7], 2, 543.
[6] Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 245 ; Kremers, *loc. cit.* ; Jones and Getman, *Zeitsch. physikal. Chem.*, 1904, 49, 405.
[7] Jones and Getman, *loc. cit.*
[8] Jones and Caldwell, *Amer. Chem. J.*, 1901, 25, 358 ; Jones and Getman, *loc. cit.*
[9] Jones and Lindsay, *Amer. Chem. J.*, 1902, 28, 352.
[10] Croft, *J. prakt. Chem.*, 1856, [1], 68, 402.
[11] Tassilly, *Ann. Chim. Phys.*, 1899, [7], 17, 117 ; *Compt. rend.*, 1896, 122, 82.
[12] Biltz, *Zeitsch. Elektrochem.*, 1920, 26, 374.
[13] Hüttig, *Zeitsch. anorg. Chem.*, 1922, 124, 322.
[14] Mosnier, *Ann. Chim. Phys.*, 1897, [7], 12, 399.
[15] Meyer, *Zeitsch. anorg. Chem.*, 1902, 30, 120   See Calcium Periodides.

Salt.	Remarks.	Authority.
$SrI_2.ZnI_2 9H_2O$	.	Ephraim and Model, *Zeitsch anorg. Chem.*, 1910, **67**, 379.
$SrI_2.CdI_2 8H_2O$	..	Jones and Caldwell, *Amer. Chem. J.*, 1901, **25**, 356.
$SrI_2.HgI_2$ $SrI_2.2HgI_2$ $SrI_2 3HgI_2$	..	Boullay, *Ann. Chim Phys.*, 1827, [2], **34**, 352.
$SrI_2.HgI_2.8H_2O$ $SrI_2 5HgI_2 8H_2O$	Density, 3·22–3 36 Long prisms of density, 4·66.	Duboin, *Compt. rend*, 1906, **142**, 573.
$SrI_2.2Hg(CN)_2.6H_2O$	..	Custer, *Arch. Pharm*, 1848, [2], **56**, 1.
$SrI_2 2PbI_2.7H_2O$	Reddish octahedral crystals which lose water at 100° C. and become bright red.	Mosmer, *Ann. Chim. Phys.*, 1897, [7], **12**, 398.

The dissociation constant of strontium tetra-iodide in aqueous solutions has been determined by distribution methods. For a 0·1246 molar solution of strontium iodide the dissociation constant "k" is about 0·00097 at 25° C.,[1] when all concentrations are expressed in gram-molecules per litre. The existence of periodides in nitrobenzene solution up to the ennea-iodide, SrI_{18}, has also been demonstrated.[2]

Mixed Halides of Strontium.—Strontium fluorochloride,[3] $SrF_2.SrCl_2$, of density 4·18 at 18° C., or 4·616,[4] fluorobromide, $SrF_2.SrBr_2$, density 4·06,[5] and fluoro-iodide, $SrF_2.SrI_2$, density 4·5,[5] have been isolated. They are crystalline compounds readily decomposed by water. The melting-point of the fluorochloride is 962° C.[6]

Mixed Perhalides of Strontium.—Iodine dissolves more readily in solutions of strontium chloride, bromide, or iodide, than in pure water, probably due to the formation of perhalogen compounds in solution.[7]

Solvent.	Water.	10 per cent solution of		
		$SrCl_2$.	$SrBr_2$.	SrI_2.
Temperature, ° C.	Ordinary temp.	18·5	13·5	13·5
Grams iodine per 100 c.c.	0·0142	0·066	0·270	6·616

It will be noticed that the solubility in the iodide solution is by far the greatest.

[1] Herz and Bulla, *Zeitsch. anorg. Chem.*, 1911, **71**, 254. (Recalculated. See Calcium Periodides.)

[2] Dawson and Goodson, *Trans. Chem. Soc.*, 1904, **85**, 796.

[3] Defacqz, *Ann. Chim. Phys.*, 1904, [8], **1**, 337; Poulenc, *ibid.*, 1894, [7], **2**, 29.

[4] Winter, *Dissert.*, Leipzig, 1913, *J. Chem. Soc.*, 1914, **106**, Abs. ii, 126.

[5] Defacqz, *loc. cit.*

[6] Winter, *loc. cit.*; see also Plato, *Zeitsch. physikal. Chem.*, 1907, **58**, 355.

[7] Meyer, *ibid.*, 1902, **30**, 113.

OXYHALOGEN DERIVATIVES OF STRONTIUM.

Strontium Oxychloride.—By heating a saturated solution of strontium chloride with strontium hydroxide, filtering, and cooling, pearly crystalline plates of composition $SrCl_2.SrO.9H_2O$ are obtained. On drying *in vacuo* the monohydrate is formed. There are probably also other hydrates with 12, 14, and 15 molecules of water of crystallisation respectively.[1]

Strontium Hypochlorite.—Dry strontium hydroxide, unlike calcium hydroxide, is unaffected by chlorine. With the crystalline hydrated strontium hydroxide, however, chloride and chlorate mixed with a little hypochlorite are obtained.[2]

Strontium Chlorite, $Sr(ClO_2)_2$, is obtained by the action of chlorous acid on strontium hydroxide, followed by rapid evaporation, first over a flame until a skin is formed, and then *in vacuo*. It separates as a deliquescent salt which is decomposed above 200° C., giving a mixture of chloride and chlorate.[3] It may also be formed by treating the precipitated peroxide with chlorine dioxide. The product explodes on percussion.[4]

Strontium Chlorate, $Sr(ClO_3)_2$, is obtained by the decomposition of strontium carbonate with chloric acid,[5] or by passing chlorine into a hot solution of strontium hydroxide, or over solid crystalline hydroxide.[2] It forms anhydrous crystals of density 3·152,[6] non-deliquescent, and readily soluble in water but not in alcohol.[7] Potilitzin[8] found several modifications of the anhydrous chlorate. Transparent rhombic octahedra separate at room temperature, but from a saturated solution cooled to −10° C. small monoclinic crystals are obtained. A third form separates in long prisms or scales at ordinary temperatures from a supersaturated solution of a certain concentration, and a fourth at 70°–90° C. in long rhombic prisms. On heating to 290° C., slow evolution of oxygen sets in, and after 10 per cent. has been given off, the mass fuses.

By cooling a 59 per cent. solution to −40° C., needle-shaped crystals of a trihydrate, $Sr(ClO_3)_2.3H_2O$, are obtained. They effloresce under atmospheric conditions. If a 64 per cent. solution be cooled to −95° C. it forms a gelatinous mass of composition $Sr(ClO_3)_2.8H_2O$. Souchay mentions a pentahydrate.[9]

Strontium Perchlorate, $Sr(ClO_4)_2$.—By the evaporation of a solution of strontium hydroxide in perchloric acid, strontium perchlorate is obtained as a deliquescent crystalline mass soluble in water and alcohol. The alcohol solution burns with a crimson flame.[10] The salt is also formed when strontium chlorate is heated just above 290° C. A mixture of perchlorate and chloride is obtained, the maximum amount of the

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[1] André, *Compt. rend.*, 1881, **93**, 58; *Ann. Chim. Phys.*, 1884, [6], **3**, 76; Tassilly, *ibid.*, 1899, [7], **17**, 62.

[2] Konigel-Weisberg, *Ber.*, 1879, **12**, 511.

[3] Millon, *Ann. Chim. Phys.*, 1843, [3], **7**, 327.

[4] Levi, *Gazzetta*, 1922, **52**, i, 417.

[5] Vauquelin, *Ann. Chim.*, 1815, [1], **95**, 97.

[6] Schröder, *Jahresber.*, 1879, 31.

[7] Potilitzin, *J. Russ. Phys. Chem. Soc*, 1889, **1**, 451; see also Wächter, *J. prakt. Chem.*, 1843, [1], **30**, 324; Souchay, *Annalen*, 1857, **102**, 381.

[8] Potilitzin, *loc. cit.*

[9] Souchay, *loc. cit.*

[10] Sérullas, *Ann. Chim. Phys.*, 1831, [2], **46**, 304.

former being present when three-quarters of the chlorate has been decomposed.[1]

The salt crystallising at 0° C. probably contains 4 molecules of water. At about 25° C. there is a dihydrate, and at 37° C., approximately, a compound, $3Sr(ClO_4)_2.2H_2O$. It is possible that there may also be a monohydrate.[2]

Strontium Oxybromide.—By boiling a concentrated solution of strontium bromide with strontium hydroxide, filtering, and cooling, prismatic crystals of composition $SrBr_2.SrO.9H_2O$ are obtained.[3] On heating to 120° C. a trihydrate is formed.

Strontium Hypobromite is probably formed by the action of bromine on strontium hydroxide in the cold.[4]

Strontium Bromate, $Sr(BrO_3)_2$, may be obtained by dissolving strontium carbonate in bromic acid.[5] It is also produced by the action of bromine on a hot solution of strontium hydroxide, but it is difficult to separate from the bromide, which is formed at the same time. It crystallises in rhombic prisms as the monohydrate, $Sr(BrO_3)_2.H_2O$, isomorphous with barium chlorate[6] and of density 3·773, but loses its water at 120° C. It begins to decompose at 240° C., losing oxygen and bromine, and leaving a residue of strontium oxide and bromide. It is soluble in three times its weight of water.[5]

Strontium Oxyiodide.—Tassilly obtained this compound by pouring a very concentrated solution of the iodide over a solution saturated with the hydroxide in the cold. After several days, crystalline needles of composition $2SrI_2.5SrO.30H_2O$ separated out.[7]

Strontium Iodate, $Sr(IO_3)_2$, may be formed by the action of iodic acid on strontium carbonate,[8] by the action of iodine on a hot solution of strontium hydroxide, or by the precipitation of a soluble strontium salt with an alkali iodate.[9] It crystallises in the anhydrous form from nitric acid solution between 70° and 80° C. It is precipitated from dilute boiling solutions in long opaque white needles of the monohydrate, $Sr(IO_3)_2.H_2O$,[9] and at ordinary temperatures as the hexahydrate, $Sr(IO_3)_2.6H_2O$.[9] The water of crystallisation is removed at 180° C., and further heating decomposes it into a mixture of oxide and iodide. One part of the salt dissolves in 342 parts of water at 15° C., and in 100 parts at 100° C. It is insoluble in sulphuric acid and decomposed by hydrochloric acid with the evolution of chlorine.

Strontium Periodate, $Sr(IO_4)_2.6H_2O$, is obtained by solution of strontium carbonate in excess of periodic acid and evaporation over sulphuric acid in the cold. It separates in large monoclinic crystals with 6 molecules of water. By dehydration over sulphuric acid the dihydrate is formed.[10] The aqueous solution has an acid reaction.

If periodic acid be practically neutralised with strontium carbonate,[10]

[1] Potilitzin, loc. cit.
[2] Willard and Smith, J. Amer. Chem. Soc , 1923, 45, 286.
[3] Tassilly, Compt. rend., 1895, 120, 1338; 1896, 122, 812; Ann. Chim. Phys., 1899, [7], 17, 63.
[4] Balard, Ann. Chim. Phys., 1826, [2], 32, 363.
[5] Rammelsberg, Pogg. Annalen, 1841, 52, 87.
[6] Rammelsberg, ibid., 1853, 90, 18.
[7] Tassilly, Ann. Chim. Phys., 1899, [7], 17, 66.
[8] Gay-Lussac, Ann Chim., 1814, [1], 91, 5; Millon, Ann. Chim. Phys., 1843, [3], 9, 418.
[9] Rammelsberg, Pogg. Annalen, 1838, 44, 575; Ditte, Ann. Chim. Phys., 1890, [6], 21, 150.
[10] Rammelsberg, Ber., 1868, 1, 70; Jahresber., 1868, 164.

or if strontium hydroxide be precipitated with sodium periodate,[1] an insoluble basic salt of composition $SrO.Sr(IO_4)_2.4$ or $3H_2O$ is formed.

STRONTIUM AND MANGANESE.

Strontium Manganite is formed in the same way as the calcium compounds, and the composition varies with the temperature of formation. $SrO.MnO_2$ is obtained above 1100° C. and below 1000° C., and $SrO.2MnO_2$ between these temperatures. There are also the compounds $SrO.5MnO_2$ and $SrO.2MnO_2$.[2]

Strontium Manganate is a greenish-blue powder insoluble in water.[3] It is formed by heating the manganite to a very high temperature— about 1600° C.[4]

Strontium Permanganate, $Sr(MnO_4)_2.4H_2O$, has been mentioned by various investigators.[5] It is very deliquescent,[6] and is decomposed by heat.[7] Its electrical conductivity in solution has been determined by Franke.[8]

STRONTIUM AND OXYGEN.

Strontium Suboxide, Sr_2O, is probably formed in the same way as barium suboxide, by the action of magnesium or aluminium on the oxide. It is less stable than the barium compound, and more readily gives crystallised strontium.[9]

Strontium Oxide, SrO, can be obtained by heating strongly the carbonate, hydroxide, or nitrate. The first of these requires a higher temperature for decomposition than calcium carbonate. It may also be formed by the direct combination of strontium and oxygen, the heat evolved being 139·64 Cal.[10] or 141·2 Cal.[11] Commercially the chief source of the oxide is the sulphate, celestine. Various methods of treatment are possible. The sulphate may be calcined with carbon to form the sulphide and the latter transformed into the hydroxide by the action of a base and again calcined ; or the sulphate may be heated in a current of water vapour and carbon monoxide;[12] or, finally, it may be fused with sodium carbonate under pressure, and the resulting carbonate calcined.[13] The oxide has also been prepared by heating the carbonate with the carbide.[14]

As usually obtained, strontium oxide is a white amorphous solid of density varying from 3·93 to 4·61, depending upon the method of preparation.[15] It forms cubical crystals, however, of density 4·75 when

[1] Langlois, *Ann. Chim. Phys.*, 1852, [3], 34, 267.

[2] Risler, *Bull. Soc. chim.*, 1878, [2], 30, 110 ; Rousseau, *Compt. rend.*, 1885, 101, 167 ; 1886, 102, 425, 616 ; 1887, 104, 786 ; 1893, 116, 1060 ; Dufau, *Ann. Chim. Phys.*, 1897, [7], 12, 257.

[3] Chevillot and Edwards, *Ann. Chim. Phys.*, 1818, [2], 8, 337.

[4] Rousseau, *Compt. rend.*, 1886, 102, 425, 615.

[5] Chevillot and Edwards, *loc. cit.* ; Mitscherlich, *Pogg. Annalen*, 1832, 25, 287.

[6] Mitscherlich, *loc. cit.*

[7] Rousseau, *Compt. rend.*, 1887, 104, 786.

[8] Franke, *Zeitsch. physikal. Chem.*, 1895, 16, 463.

[9] Guntz, *Ann. Chim. Phys.*, 1907, [8], 10, 447. See Barium Suboxide.

[10] de Forcrand, *Compt. rend.*, 1911, 152, 27.

[11] Guntz and Roederer, *ibid.*, 1906, 142, 400.

[12] Jacquemin, *ibid.*, 1858, 46, 1164.

[13] See Terres and Brückner, *Zeitsch. Elektrochem.*, 1920, 26, 25.

[14] Frank, German Patent, 135330 (1901).

[15] Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415 ; Brügelmann, *Zeitsch. anal. Chem.*, 1890, 29, 126.

prepared by very slow calcination of the nitrate.[1] The transparent liquid, obtained by fusion in the electric arc at about 3000° C., which is more easily accomplished than in the case of calcium oxide, forms on cooling a confused mass of crystals.[2] A crystallised specimen may also be obtained by heating a mixture of strontium carbonate with lithium carbonate.[3]

Sulphuretted hydrogen reacts with strontium oxide in the cold, forming water and sulphur with considerable heat evolution.[4] Sulphur dioxide[5] and carbon dioxide[6] react with strontium oxide when heated, but not in the cold. In the case of carbon dioxide the reaction may become so vigorous that the product is incandescent, and a temperature of 1050° C. may be reached.

Strontium oxide dissolves in fused strontium chloride, one molecule of the former saturating three of the latter.[7]

From a consideration of heat phenomena, de Forcrand concluded that the molecule of strontium oxide should be regarded as a condensed molecule with the formula $(SrO)_n$.[8]

Strontium Hydroxide, $Sr(OH)_2$.—Strontium oxide may be " slaked " by water producing the hydroxide (see Calcium). The heat generated by this reaction is 19 44 Cal.[8] Strontium hydroxide may be obtained as an intermediate product in the formation of strontium oxide from strontium minerals. It is prepared, for example, by the decomposition of strontium sulphide,[9] or carbonate,[10] by superheated steam at 500°–600° C.,[9] by the oxidation of the sulphide in a current of air in the presence of Weldon mud as catalyst,[11] or by the action of sodium sulphate and carbon on the sulphide.[12] It may also be formed in the dissolved state by the electrolysis of strontium chloride and sulphide solution with an iron or carbon anode.[13]

The density of strontium hydroxide is 3·625.[14]

By heating at 850° C. the oxide is again formed.[8] *In vacuo* the greater part of the water is removed below 540° C., and dehydration is complete at 710° C.[15]

The following values have been found for the vapour pressure of the hydroxide at different temperatures [16] :—

Temperature, °C.	452	488	524	561	597	634	670	706	742	778
Pressure in mm. Hg	9·2	17·4	31·5	55	92	149	234	355	526	760

The heat of solution of strontium hydroxide is 19·43 Cal.[8] It is

[1] Brugelmann, *loc. cit.*; *Wied. Annalen*, 1877, 3, 466; 1878, 4, 277; *Zeitsch. anorg. Chem.*, 1895, 10, 415; 1908, 59, 248.
[2] Moissan, *Compt. rend.*, 1892, 115, 1034; *Ann. Chim. Phys.*, 1895. [7], 4, 136.
[3] Lebeau, *ibid.*, 1905, [8], 6, 433.
[4] Schumann, *Annalen*, 1877, 187, 311.
[5] Birnbaum and Wittich, *Ber.*, 1880, 13, 651.
[6] Scheibler, *ibid.*, 1886, 19, 1973; Raoult, *Compt. rend.*, 1881, 92, 1110.
[7] Arndt, *Ber.*, 1907, 40, 427.
[8] de Forcrand, *Compt. rend.*, 1908, 147, 165.
[9] Haber and Poindexter, *J. Soc. Chem. Ind.*, 1917, 36, 385.
[10] Leplay, *Dingl. poly. J.*, 1884, 254, 436.
[11] Pattinson, *Ber.*, 1886, 19, Ref., 516.
[12] Mactear, *Dingl. poly. J.*, 1886, 262, 287.
[13] Brochet and Ranson, English Patent, 1849 (1901).
[14] Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 417.
[15] Herzfeld and Stiepel, *Zeitsch. Rübenzuckerind.*, 1898, 833.
[16] Johnston, *Zeitsch. physikal. Chem.*, 1908, 62, 330; see also *J. Amer. Chem. Soc.*, 1908, 30, 1357.

more soluble than the calcium compound, and produces a strongly basic solution. The following values have been given for the solubility [1] :—

Temperature, °C. .	0	20	40	50	65	75	85	101·2
Grams SrO per 100 parts solution .	0·35	0·69	1 48	2 13	3·74	5 29	9·08	19 34

In the presence of bases the solubility is diminished to a greater extent than can be explained by the decrease of dissociation. The influence of strontium salts is very small, probably indicating the formation of compounds, basic salts, in solution. In solutions of strontium nitrate the solubility increases with the concentration of the latter, but no basic salts have been isolated.[2] It is readily soluble in cane sugar solutions in which it forms strontium saccharate.[3]

The molecular conductivities of strontium hydroxide solutions have been measured by Ostwald.[4]

Under the influence of the cathode rays, strontium hydroxide gives a beautiful deep blue phosphorescence.[5]

Hydrates of Strontium Hydroxide.—Strontium hydroxide octahydrate, $Sr(OH)_2.8H_2O$, separates as tetragonal crystals,[6] of density 1·396,[7] from solutions at ordinary temperatures.[8] Berthelot ascribed to it the formula $Sr(OH)_2.9H_2O$.[9] From vapour pressure measurements Lescœur concluded that there was a higher hydrate than the octahydrate,[10] and there also appear to be a hepta-[11] and a di-hydrate.[12] The heat of solution of the octahydrate is $-14\ 27$ Cal.,[13] and the heat of hydration from the hydroxide 24·60 Cal.[13]

The monohydrate, $Sr(OH)_2.H_2O$, is formed by heating the octahydrate for two hours in a current of dry hydrogen at 45°–50° C.,[13] by leaving *in vacuo* over sulphuric acid,[10] or by passing first air saturated with water vapour, and then dry air, at ordinary temperatures over strontium oxide.[14] At 95° C. it loses its water of hydration, forming the simple hydroxide.[15] The heat of solution of the monohydrate is 5·26 Cal.,[13] and the heat of hydration from the hydroxide 5·06 Cal.[13] It absorbs carbon dioxide with complete transformation into the carbonate.[14]

Strontium oxide forms compounds with mannitol.[16]

[1] Scheibler, *Zeitsch. anal. Chem* , 1882, **21**, 561.
[2] Parsons and Perkins, *J. Amer. Chem. Soc.,* 1910, **32**, 1387.
[3] Scheibler, *Dingl. poly. J.,* 1883, **248**, 426.
[4] Ostwald, *J. prakt. Chem.,* 1886, [2], **33**, 357.
[5] Crookes, *Proc. Roy. Soc.,* 1881, **32**, 206.
[6] Foullon, *Zeitsch. Kryst. Min.,* 1887, **12**, 531.
[7] Filhol, *loc. cit.*
[8] Souchay and Lenssen, *Annalen,* 1856, **99**, 45 ; Bloxam, *Jahresber.,* 1859, 131 ; de Forcrand, *loc. cit.*
[9] Berthelot, *Jahresber.,* 1873, 79.
[10] Lescœur, *Ann. Chim. Phys.,* 1890, [6], **19**, 65.
[11] Müller-Erzbach, *Ber.,* 1887, **20**, 1628.
[12] Johnston, *Zeitsch. physikal. Chem.,* 1908, **62**, 345
[13] de Forcrand, *loc. cit.*
[14] Heyer, *Ber.,* 1886, **19**, 2684.
[15] de Forcrand, *loc. cit.* ; Herzfeld and Stiepel, *loc. cit.*
[16] Ubaldini, *Ann. Chim. Phys.,* 1859, [3], **57**, 213.

Uses of Strontium Hydroxide.—The use of strontia in the sugar industry for the purification of sugar by the precipitation of di-strontium saccharate was first patented by Dubrunfaut and Leplay in 1849, and introduced into the German beet-sugar factories by Fleicher in 1869. The process was modified and improved by Scheibler.[1]

Strontium Peroxide, SrO_2.—Similarly to calcium peroxide, strontium peroxide was first obtained as a white crystalline precipitate in the hydrated form, $SrO_2.8H_2O$, by the action of hydrogen peroxide or sodium peroxide on strontium hydroxide.[2] It is also formed when an alkali reacts with a strontium salt solution containing hydrogen peroxide.[3] By heating to 130° C. in a current of dry air, or by drying *in vacuo*, the anhydrous compound is obtained,[4] but it cannot be completely freed from water without partial decomposition.[5] The anhydrous peroxide may be prepared directly by precipitating from very concentrated solutions above 50° C.[3] Very large pressures are required in order to make strontium oxide combine directly with oxygen. Combination under a pressure of 76 atmospheres of oxygen is possible, but the maximum yield, 15–16 per cent. of peroxide, is obtained at about 400° C. under a pressure of 98 atmospheres.[6]

The heat of formation from strontium oxide and oxygen is 10·875 Cal.,[5] or from metallic strontium and oxygen 153·07 Cal.[7]

At red heat strontium peroxide melts and gives off oxygen. It is a white powder, only slightly soluble in water, by which it is partially decomposed, but soluble in acids. Anhydrous commercial strontium oxide contains 85 per cent. of strontium peroxide and 15 per cent. of strontium hydroxide, and has a density of 0·546. It is very stable in a dry atmosphere, and may be heated to 150° C. without loss of available oxygen.[8]

Hydrates of Strontium Peroxide.—The octahydrate is precipitated at ordinary temperatures from dilute solutions of strontium hydroxide and hydrogen peroxide.[3] It has been suggested that the compound formed contains 9 molecules of water of crystallisation.[5] The heat of hydration is 20·48 Cal.[5] Hydrates containing 10 and 12 molecules of water have been mentioned.[9]

Strontium Diperoxyhydrate, $SrO_2.2H_2O_2$, is obtained by the action of concentrated hydrogen peroxide on the octahydrate at low temperatures.[3] It is possible that a monoperoxyhydrate is also formed, but in a very impure state.[10]

[1] Scheibler, *Dingl. poly. J.*, 1882, **245**, 430, 465, 506; **248**, 426; *Zeitsch. Ruben-zuckerind.*, 1882, 8, 49; *Ber.*, 1883, **16**, 984; Patents in 1881, 1882, 1883.

[2] Thénard, *Ann. Chim. Phys.*, 1818, [2], 8, 306; Conroy, *Chem. News*, 1873, **27**, 291; *J. Chem. Soc.*, 1873, **26**, 808; Schöne, *Ber.*, 1873, 6, 1172.

[3] Riesenfeld and Nottebohm, *Zeitsch. anorg. Chem.*, 1914, **89**, 405.

[4] Schöne, *loc. cit.*

[5] de Forcrand, *Compt. rend.*, 1900, **130**, 1017.

[6] Fischer and Ploetze, *Zeitsch. anorg. Chem.*, 1912, **75**, 10; see also Pierce, English Patent, 130840 (1918).

[7] de Forcrand, *Ann. Chim. Phys.*, 1908, [8], **15**, 433.

[8] von Foregger and Philipp, *J. Soc. Chem. Ind.*, 1906, **25**, 298.

[9] Conroy, *loc. cit.*

[10] Schöne, *Annalen*, 1878, **192**, 282.

STRONTIUM AND SULPHUR.

Strontium Monosulphide, SrS, may be obtained by methods similar to those employed in the preparation of calcium sulphide ; for example :—

1. By the action of sulphuretted hydrogen on strontium carbonate or oxide at red heat, the product being cooled in hydrogen.[1]

2. By reduction of strontium sulphate by carbon,[2] or by heating in a reducing flame.[3]

3. By the action of carbon disulphide on strontium carbonate, preferably in an atmosphere of sulphuretted hydrogen.[4]

4. By heating strontium thiosulphate.[5]

5. By the reduction of strontium sulphate with hydrogen.[6] A certain amount of oxide is also formed by this method.

As ordinarily prepared, strontium sulphide is a white or greyish amorphous powder of density 3·35, but by heating in the electric furnace for a few minutes, or by preparing it by the reduction of strontium sulphate by carbon in the electric furnace, it is obtained as cubical crystals, and possibly also as regular octahedra of density 3·7.[7]

The heat of formation of strontium sulphide from its elements is 99·2 Cal.,[8] or, if the sulphur is in the gaseous state, 113·0 Cal.[9] The heat of solution is 7·4 Cal.

In contact with water it forms strontium hydrosulphide and hydroxide.[10] Carbon, at high temperatures, transforms it into the carbide. Fluorine, oxygen, non-metallic chlorides, and oxidising agents readily attack it, but it is not attacked by hydrogen even at high temperatures. On gently heating with water vapour, sulphuretted hydrogen is given off.[7]

Phosphorescent Strontium Sulphide.—Much of what has been written with regard to the phosphorescence of calcium sulphide applies also to strontium sulphide, and references to the literature of phosphorescent sulphides will be found under the former heading.[11]

Strontium Hydrosulphide, $Sr(SH)_2$, is formed in solution by saturating a strontium hydroxide solution with sulphuretted hydrogen, preferably at 65°–70° C.,[12] or by the action of a solution of sulphuretted hydrogen on strontium sulphide. On evaporation *in vacuo* large prismatic crystals, of composition $Sr(SH)_2.4H_2O$, are obtained. It is stable in dry air, and on heating melts in its water of crystallisation.[13] The following values of the solubility at different temperatures are given

[1] Sabatier, *Ann. Chim. Phys.*, 1881, [5], 22, 6 ; Mourelo, *Compt. rend.*, 1898, 125, 775.

[2] Mourlot, *Ann. Chim. Phys.*, 1899, [7], 17, 522.

[3] Haber and Poindexter, U.S. Patent, 1213375 (1917), see *J. Soc. Chem. Ind.*, 1917, 36, 385.

[4] Schöne, *Pogg. Annalen*, 1861, 112, 193.

[5] Kern, *Chem. News*, 1875, 32, 137.

[6] Schumann, *Annalen*, 1877, 187, 304.

[7] Mourlot, *loc. cit.* ; *Compt. rend.*, 1898, 127, 408.

[8] Sabatier, *loc. cit.*

[9] de Forcrand, *Ann. Chim. Phys.*, 1911, [8], 24, 272.

[10] Rose, *Pogg. Annalen*, 1842, 55, 415, 533 ; de Clermont and Frommel, *Ann. Chim. Phys.*, 1879, [5], 18, 203.

[11] Mourelo, *Compt. rend.*, 1897, 124, 1237, 1521 ; 1898, 126, 420, 904 ; 127, 229, 372 ; 1899, 128, 427, 557 ; 129, 1236 ; 1915, 160, 174.

[12] Terres and Brückner, *Zeitsch. Elektrochem.*, 1920, 26, 25.

[13] Rose, *loc. cit.*

by Terres and Bruckner,[1] but no measurements of the pressure of sulphuretted hydrogen are recorded :—

Temperature, °C.	0	20	40	60	80	100
Grams $Sr(SH)_2$ in 100 grams solution	27·5	29·7	31·6	33·2	35·6	37·8

Strontium Polysulphides.—By boiling strontium monosulphide with sulphur and water, a tetra- and possibly also a penta-sulphide are formed.

Strontium Tetrasulphide, SrS_4.—On evaporating *in vacuo* at 15° C. to the consistency of a syrup the solution obtained with three molecules of sulphur to one of strontium sulphide, and keeping for several days at a fairly low temperature, red prismatic crystals of the compound $SrS_4.6H_2O$ are obtained.[2] It is very hygroscopic, dissolves readily in water and alcohol—the solution oxidising in the air—and melts at 25° C. At 100° C. it loses 4 molecules of water, giving a solid yellow mass of composition $SrS_4.2H_2O$. The same substance is formed as bright yellow crystals by evaporating the original syrup at a somewhat higher temperature, namely 25° C. instead of 15° C.

Strontium Oxysulphide.—By exposure of the tetrasulphide crystals to the air, red crystals of an oxysulphide, $SrO.SrS_4.12H_2O$,[3] are obtained. Geuther, however, regarded them as mixed crystals of strontium thiosulphate and an otherwise unknown disulphide.[4] By the action of sulphuretted hydrogen on strontium oxide the compound $2SrS.SrO$ is formed.[5]

Strontium Thiosulphate, SrS_2O_3, may be formed by boiling sulphur with strontium hydroxide and precipitating with alcohol,[6] by the action of sulphur dioxide on a hot solution of strontium sulphide,[7] or, finally, by precipitating a hot solution of strontium nitrate with sodium thiosulphate.[8] The thiosulphate crystallises out on cooling or on adding alcohol.[8] It forms large hexagonal crystals of composition $SrS_2O_3.5H_2O$,[9] more stable than the corresponding calcium salt. It is soluble in 4 parts of water at 13° C., and in 1·75 parts at 100° C.[7] It loses 4 molecules of water at 100° C.[9] Dried at 200° C., it has the composition $2SrS_2O_3.H_2O$.[9] Further dehydration is accompanied by decomposition, and, on strongly heating, the salt forms a phosphorescent mixture of sulphide, sulphate, and sulphur according to the equation—

$$4SrS_2O_3 = SrS + 3SrSO_4 + 4S.[10]$$
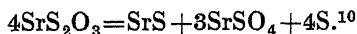
Clarke[11] gives the density of a hexahydrate[12] as 2·1566 and 2·1991 at 17° C.

[1] Terres and Bruckner, *Zeitsch. Elektrochem.*, 1920, **26**, 25.
[2] Schöne, *Pogg. Annalen*, 1862, **117**, 58.
[3] Schone, *loc. cit.*; but see Gay-Lussac, *Ann. Chim. Phys.*, 1820, [2], **14**, 362.
[4] Geuther, *Annalen*, 1884, **224**, 198.
[5] Schumann, *ibid.*, 1877, **187**, 311.
[6] Grotthuss, *Schweigger's J.*, 1813, **9**, 332.
[7] Herschell, *Edin. Phil. J.*, **1**, 8, 396; **2**, 154; *Ann. Chim. Phys.*, 1820, [2], **14**, 356.
[8] Kessler, *Pogg. Annalen*, 1848, **74**, 282; see also Kern, *Chem. News*, 1875, **32**, 137.
[9] Letts, *J. Chem. Soc.*, 1870, **23**, 428.
[10] Mourelo, *Compt. rend.*, 1898, **126**, 420; **127**, 372. According to Rammelsberg sulphite is also formed, Rammelsberg, *Pogg. Annalen*, 1842, **56**, 301.
[11] Clarke, *Amer. J. Sci.*, 1877, [3], **14**, 281; *Jahresber.*, 1877, 43.
[12] Kessler, *loc. cit.*

Strontium Hyposulphite, SrS_2O_4, is obtained by the action of sulphur dioxide on strontium hydride at a pressure above one atmosphere. Hydrogen is liberated at the same time. A solution of the salt is a powerful reducing agent.[1]

Strontium Sulphite, $SrSO_3$, may be obtained by the precipitation of strontium chloride with an alkali sulphite.[2] It is also formed when strontium oxide is heated with sulphur dioxide at 230°–290° C.[3] Several weeks are required in order to complete the reaction. The salt is anhydrous and readily crystallises in flattened prisms.[4] It is slowly oxidised to sulphate by air. On heating, it is transformed into a phosphorescent mixture of strontium sulphide and sulphate.[5] The solubility of the sulphite in water is less than that of the sulphate, being only 33 mgm. per litre at ordinary temperatures.[6]

Strontium Dithionate, SrS_2O_6, is formed by neutralising dithionic acid with strontium hydroxide.[7] It is isomorphous with the corresponding calcium salt. It may also be obtained by acting upon strontium nitrate with sodium dithionate in solution, cooling slowly, and evaporating the solution at or above 50° C., when a monohydrate is obtained.[8] At ordinary temperatures it crystallises with 4 molecules of water in large hexagonal plates, which are stable in air and rotate the plane of polarisation to the left.[9] The solution is inactive. The salt loses water of crystallisation at 78° C.[10] It dissolves in 4·5 parts of water at 16° C. and in 2·5 parts at 100° C.,[11] but is not very soluble in alcohol. The heat of solution in water is −9·250 Cal.[12]

Strontium Tetrathionate, SrS_4O_6, is obtained by the addition of strontium acetate to tetrathionic acid, and subsequent precipitation with absolute alcohol.[8] It is also formed by the oxidation of strontium thiosulphate with iodine. When a solution of strontium tetrathionate is evaporated, thin prismatic crystals containing 6 molecules of water of crystallisation separate. They are not very stable, and the solution has a tendency to split up into sulphur, sulphur dioxide, and strontium sulphate.

Strontium Sulphate, $SrSO_4$, occurs naturally as the mineral *celestine*, or associated with barium as *barytocelestine*. Celestine forms rhombic crystals, sometimes of a blue colour, hence its name. Certain waters contain strontium sulphate in solution.[13] It may be obtained as a microcrystalline precipitate by the action of sulphuric acid on a strontium salt, or in larger crystals by the fusion of an excess of strontium chloride with potassium sulphate,[14] by heating the precipitated sulphate

[1] Moissan, *Compt. rend*, 1902, **135**, 653.

[2] Röhrig, *J. prakt. Chem.*, 1888, [2], **37**, 232 ; Rammelsberg, *Pogg. Annalen*, 1846, **67**, 249 ; Muspratt, *Annalen*, 1844, **50**, 274.

[3] Birnbaum and Wittich, *Ber.*, 1880, **13**, 651.

[4] Rammelsberg, *loc. cit.* ; see also Röhrig, *loc. cit.*

[5] Forster, *Pogg. Annalen*, 1865, **133**, 94, 228 ; Mourelo, *Compt. rend.*, 1898, **126**, 420.

[6] Hinds, *J. Amer. Chem. Soc.*, 1911, **33**, 510.

[7] Welter and Gay-Lussac, *Ann. Chim. Phys.*, 1819, [2], **10**, 314.

[8] Kessler, *Annalen*, 1848, **68**, 231 ; *Pogg. Annalen*, 1848, **74**, 274.

[9] Bodländer, *Zeitsch. Kryst. Min.*, 1884, **9**, 309 ; see also Pape, *Pogg. Annalen*, 1865, **125**, 513 ; 1870, **139**, 224 ; Bichat, *Bull. Soc. chim.*, 1873, [2], **20**, 436.

[10] Pape, *Pogg. Annalen*, 1865, **125**, 513.

[11] Heeren, *ibid.*, 1826, **7**, 177.

[12] Thomsen, *Thermochemistry*, English translation by Burke (Longmans, Green & Co.), 1908, p. 50.

[13] Bloxam, *Chem. News*, 1884, **49**, 3.

[14] Manross, *Annalen*, 1852, **82**, 350.

with dilute hydrochloric acid in a sealed tube at 150° C.,[1] by precipitating very slowly from extremely dilute solutions,[2] or, finally, by evaporating the sulphuric acid solution of strontium sulphate to dryness.[3] The density of the precipitated sulphate is 3·7–3·8,[4] of natural celestine 3·92–3·96, and of artificial 3·927.[5] The specific heat of celestine is 0·135.[6]

Strontium sulphate melts at 1605° C.,[7] but becomes basic through loss of sulphur trioxide.[8] There is a transition point at 1152° C. to a-SrSO$_4$, isomorphous with a-CaSO$_4$ and a-BaSO$_4$, with both of which it is miscible in all proportions. Below this transition point strontium sulphate is completely miscible with barium sulphate, but only partially with calcium sulphate.[9]

Carbon, carbon monoxide, and other reducing agents reduce it at red heat, forming the sulphide.[10] On boiling with sodium carbonate solution it is transformed into strontium carbonate.[11]

Under the influence of the cathode rays, strontium sulphate shows a pale lilac fluorescence, which is not materially affected by the presence of manganese, but is changed to a brilliant orange by bismuth.[12]

Strontium sulphate is only slightly soluble in water, 1 litre of the solution at 18° C. containing 1·245 milli-equivalents, or 114·3 mgm.[13] The heat of solution is −0·3 Cal.[11] The solubility varies very little with temperature,[13] but is notably increased by the presence of acids, as is indicated by the following table [15] :—

C c. containing 1 mgm.-equiv. of Acid.	Increase in Solubility at 20° C. in mgm. SrSO$_4$ per mgm.-equivalent of Acid.			
	HCl.	HNO$_3$.	CH$_2$ClCOOH.	HCOOH.
0·2	0·29	0 73	..	..
0·5	0·96	1·46	..	..
1	1·72	2·01	0·104	0 080
2	2·20	2 44	0·133	..
10	3·25	3·22	..	..

[1] Bourgeois, *Compt. rend.*, 1887, **105**, 1072.
[2] de Schulten, *ibid.*, 1903, **136**, 1444.
[3] Gaubert, *ibid.*, 1907, **145**, 877.
[4] Filhol, *Ann. Chim. Phys.*, 1847, [3], **21**, 417; Schröder, *Pogg. Annalen*, 1859, **106**, 226.
[5] Manross, *loc. cit.*
[6] Kopp, *Annalen Suppl.*, 1864–5, **3**, 296.
[7] Grahmann, *Zeitsch. anorg. Chem.*, 1903, **81**, 257.
[8] Boussingault, *Ann. Chim. Phys.*, 1867, [4], **12**, 422.
[9] Grahmann, *Jahrb. Min.*, 1920, i, 1.
[10] See Strontium Sulphide.
[11] Herz, *Zeitsch. anorg. Chem.*, 1910, **68**, 69.
[12] de Boisbaudran, *Compt. rend.*, 1886, **103**, 468, 629; *J. Chem. Soc.*, 1887, **52**, Abs., 3, 4.
[13] Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, **64**, 129; see also Holleman, *ibid.*, 1893, **12**, 131.
[14] Thomsen, *loc. cit.*, p. 137.
[15] Ostwald and Banthisch, *J. prakt. Chem.*, 1884, [2], **29**, 52.

The solubility is diminished by dilute sulphuric acid. It is increased by alkali chlorides and nitrates,[1] by calcium salts,[2] and even by strontium salts, probably owing to the formation of a complex ion. The solubility is decreased by sulphates and alcohol.

A colloidal precipitate of strontium sulphate is obtained by precipitation from an alcoholic solution of strontium thiocyanate.[3]

Double Salts :

Salt.	Authority.
$SrSO_4.3Na_2SO_4$ . .	Calcagni, *Atti R. Accad. Lincei*, 1912, [5], 21, ii, 71.
$SrSO_4.K_2SO_4$ . .	Calcagni, *loc. cit.* See also Rose, *Jahresber.*, 1854, 292.
$2SrSO_4.K_2SO_4$ . .	Grahmann, *Zeitsch. anorg. Chem.*, 1913, 81, 257.
$SrSO_4.Ti(SO_4)_2$ . .	Weinland and Kuhl, *Zeitsch. anorg. Chem.*, 1907, 54, 253.
$SrSO_4.Sn(SO_4)_2.3H_2O$.	Weinland and Kuhl, *Ber.*, 1906, 39, 2951.
$SrSO_4.Sb_2(SO_4)_3.6H_2O$	Kuhl, *Zeitsch. anorg. Chem.*, 1907, 54, 256.

Acid Strontium Sulphate, $SrH_2(SO_4)_2$, is obtained by crystallisation from a solution of the sulphate in hot concentrated sulphuric acid. At 70° C. 14 parts of strontium sulphate dissolve in 100 of acid. On lowering the temperature, tabular rhombic crystals are obtained, and on raising it, cubes and octahedra.[4] By exposure of the crystals or the solution to the air, brilliant leaflets of the monohydrate are formed.[5]

Strontium Pyrosulphate, SrS_2O_7, is formed by the action of sulphur trioxide on strontium sulphate in a sealed tube.[6] It attracts moisture rapidly from the air and reacts vigorously with water.

STRONTIUM AND SELENIUM.

Strontium Selenide, SrSe, is obtained by the reduction of strontium selenite by hydrogen at 600° C.[7] It is a white microcrystalline substance, of density 4·38,[7] with a reddish tinge, probably due to the presence of selenium, and it is more fusible and less stable than calcium selenide.[8] It can also be prepared by heating selenium with strontium oxide or carbonate.[9] The heat of formation from the elements is 77·14 Cal.[10] The phosphorescence of strontium selenide has been studied by Pauli[11] and Kittlemann.[9]

[1] Wackenroder, *Annalen*, 1842, 41, 315 ; Virck, *Jahresber.*, 1862, 127 ; see also Wolfmann, *Chem. Zentr.*, 1897, i, 632.
[2] Raffo and Rossi, *Gazzetta*, 1915, 45, i, 45.
[3] von Weimarn, *Zeitsch. Chem. Ind. Koll.*, 1908, 3, 89.
[4] Garside, *Chem. News*, 1875, 31, 245.
[5] Schultz, *Pogg. Annalen*, 1868, 133, 137.
[6] Schulze, *Ber.*, 1884, 17, 2705.
[7] Henglein and Roth, *Zeitsch. anorg. Chem.*, 1923, 126, 227.
[8] Fabre, *Ann. Chim. Phys.*, 1887, [6], 10, 515.
[9] Kittlemann, *Ann. Physik*, 1915, [4], 46, 177.
[10] de Forcrand, *Ann. Chim. Phys.*, 1911. [8], 24, 272 ; but see Kittlemann, *loc. cit.*
[11] Pauli, *Ann. Physik*, 1912, [4], 38, 870 ; see also Calcium Selenide.

Strontium Selenite, $SrSeO_3$, is obtained by the action of an alkali selenite on a soluble strontium salt in either acid or neutral solution. Whether it is anhydrous or hydrated depends upon conditions, the two hydrated forms known being $SrSeO_3.3H_2O$ and $2SrSeO_3.7H_2O$ (?). An acid salt, $SrH_2Se_2O_6$, may also be obtained.[1]

Strontium Selenate, $SrSeO_4$, is obtained as orthorhombic crystals, similar to the celestine from Lake Erie, by fusing an alkali selenate to bright redness with sodium and strontium chlorides. It affects polarised light strongly and exhibits pleochroism. Its density is 4·25.[2]

STRONTIUM AND TELLURIUM.

Strontium Telluride.—An impure telluride is obtained by reducing strontium tellurate with hydrogen at 360° C.[3]

Strontium Tellurite, $SrTeO_3$, is obtained as a voluminous flocculent precipitate, very slightly soluble in water, by the action of an alkali tellurite on a soluble strontium salt.[4]

Strontium Tellurate, $SrTeO_4$, forms a white flocculent mass, soluble in a large excess of water, when an alkali tellurate reacts in solution with a soluble strontium salt.[4]

STRONTIUM AND CHROMIUM.

Strontium Chromate, $SrCrO_4$, may be obtained in rhombohedric scales by fusion of sodium and potassium chromates with strontium chloride.[5] It is also prepared by precipitation as a yellow crystalline powder of density 3 353.[6] Short, thick hexagonal prisms separate from very dilute solutions, and long, fine needles from concentrated.[7] The precipitation is prevented by acetic acid. One part of strontium chromate is soluble in 831 8 parts of water at 15° C.[8] It is easily soluble in all acids and also in molten sodium nitrate.[9] Fresenius determined its solubility in dilute solutions of ammonia salts and in dilute alcohol.

A solid solution of strontium chromate in barium chromate is obtained by precipitating barium chromate in a solution containing strontium chromate and acetic acid. There is an approximately constant relation between the concentration of strontium in the solution and the amount retained by the precipitate.[10]

Double Salts.—The double chromates, $SrK_2(CrO_4)_2$[11] and $Sr(NH_4)_2$ $(CrO_4)_2$,[12] are formed by acting upon a solution of a strontium salt with excess of a concentrated chromate solution. Compounds with mercuric

[1] Nilson, *Bull. Soc. chim.*, 1874, [2], **21**, 253 ; Muspratt, *J. Chem. Soc.*, 1850, 2, 60.
[2] Michel, *Compt. rend.*, 1888, **106**, 878.
[3] Henglein and Roth, *Zeitsch. anorg. Chem.*, 1923, **126**, 227.
[4] Berzelius, *Ann. Chim. Phys.*, 1835, [2], **58**, 258.
[5] Bourgeois, *Compt. rend.*, 1879, **88**, 382.
[6] Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873.
[7] Autenrieth, *Ber.*, 1904, **37**, 3882.
[8] Fresenius, *Zeitsch. anal. Chem.*, 1890, **29**, 418 ; see also Meschezerski, *ibid.*, 1882, **21**, 399.
[9] Guthrie, *Trans. Chem. Soc.*, 1885, **47**, 94.
[10] Duschak, *J. Amer. Chem. Soc.*, 1908, **30**, 1827.
[11] Gröger, *Zeitsch. anorg. Chem*, 1907, **54**, 185 ; Barre, *Compt. rend.*, 1914, **158**, 495.
[12] Gröger, *Zeitsch. anorg. Chem*, 1908, **58**, 412.

chloride and hydrochloric acid, $(SrCrO_4.3HgCl_2)_2.HCl$ [1] and $SrCrO_4.2HgCl_2.HCl$,[2] have also been prepared.

Strontium Dichromate, $SrCr_2O_7.3H_2O$, is prepared by the action of concentrated chromic acid on strontium chromate and subsequent evaporation over sulphuric acid, or by the incomplete saturation of chromic acid by calcium carbonate.[3] It is readily soluble in water, and forms large red-brown monoclinic plates which lose water at 110° C.[4]

Strontium Trichromate, $SrCr_3O_{10}.3H_2O$, is obtained by the action of excess of chromic acid on strontium chromate.[3] It forms granite-red hygroscopic crystals.

Strontium Chlorochromate, $Sr(CrO_3Cl)_2.4H_2O$, may be obtained by the action of chromyl chloride on strontium chromate in acetic acid solution.[5] It forms carmine-red hygroscopic crystals which melt in their water of crystallisation at 72° C.

STRONTIUM AND MOLYBDENUM.

Strontium Molybdate, $SrMoO_4$, analogous with the calcium salt, is obtained by precipitating strontium chloride solution with neutral sodium molybdate.[6] It may also be prepared in the form of white tetragonal pyramids of density 4·185 at 21° C. by fusing together sodium molybdate, strontium chloride, and sodium chloride.[7] Its crystalline form has been studied by Hiortdahl.[8] One part of the salt is soluble in 9600 parts of water at 17° C.[9]

An acid salt, strontium octamolybdate, $2SrO.3H_2O.20MoO_3.21H_2O$, has been described.[10]

Complex Strontium Molybdates.—By boiling a mixture of strontium nitrate and molybdoiodic acid, and then cooling, a white spongy mass of small crystals of composition $3SrO(I_2O_5.2MoO_3)_4.15H_2O$ is produced.[11] The normal molybdoiodate may be prepared by the action of the lithium salt on strontium nitrate. It is very soluble in water, and on evaporating a solution of the salt, the compound $SrO.I_2O_5.2MoO_3.3H_2O$ is obtained. There is also a sulphomolybdate.[12]

A double strontium sodium molybdoperiodate, of composition $4SrO.Na_2O.I_2O_7.12MoO_3.20H_2O$, has been described,[13] and an arseno-molybdate.[14]

STRONTIUM AND TUNGSTEN.

Strontium Tungstate, $SrWO_4$, may be obtained as a white micro-crystalline precipitate by the action of an alkali tungstate solution

[1] Imbert and Belugou, *Bull. Soc. chim.*, 1897, [3], 17, 471 ; Belugou, *ibid.*, 473.
[2] Imbert and Belugou, *loc. cit.*
[3] Preis and Rayman, *Ber.*, 1880, 13, 340.
[4] Wyrouboff, *Bull. Soc. franç. Min.*, 1891, 14, 77.
[5] Pràtorius, *Annalen*, 1880, 201, 32.
[6] Schultze, *ibid.*, 1863, 126, 49.
[7] Clarke and Marsh, *Amer. J. Sci*, 1877, [3], 14, 281.
[8] Hiortdahl, *Zeitsch. Kryst. Min.*, 1887, 12, 411.
[9] Smith and Bradbury, *Ber.*, 1891, 24, 2930.
[10] Wempe, *Zeitsch. anorg. Chem.*, 1912, 78, 321.
[11] Chrétien, *Ann. Chim. Phys.*, 1898, [7], 15, 358.
[12] Berzelius, *Pogg. Annalen*, 1826, 7, 261.
[13] Blomstrand, *Zeitsch. anorg. Chem.*, 1892, 1, 10.
[14] Pufahl, *Ber.*, 1884, 17, 217.

on strontium chloride or acetate.[1] By fusion of sodium tungstate with strontium and sodium chlorides [2] it is formed as tetragonal crystals of density 6 184 at 20° C.[3] One part of the precipitated salt dissolves in 700 parts of water at 15° C.[4] It is decomposed by heat.[5]

Several acid tungstates are known.[6]

There is a complex phosphotungstate, $2SrO.P_2O_5.12WO_3.17H_2O$.[7] and a borotungstate.[8]

A double sodium strontium tungstate may be formed by the action of a boiling sodium paratungstate solution on strontium chloride.[9]

Tungsten bronzes containing strontium may be obtained by methods similar to those employed for the preparation of the corresponding calcium compounds.[10] Potassio-strontium bronze has the composition $SrW_4O_{12}.5K_2W_4O_{12}$, and the two sodio-strontium bronzes, $SrW_4O_{12}.5Na_2W_5O_{15}$ and $SrW_4O_{12}.12Na_2W_3O_9$.

STRONTIUM AND URANIUM.

Strontium Uranate, $SrUO_4$, is obtained in small yellow crystals by fusing strontium chloride with green uranium oxide, U_3O_8,[11] and the diuranate, SrU_2O_7, by heating uranium oxide with strontium chlorate. The amorphous diuranate may be crystallised from solution in fused strontium chloride.

STRONTIUM AND NITROGEN.

Strontium Nitride, Sr_3N_2, was first obtained by heating strontium amalgam in a current of nitrogen.[12] The mercury distilled off, and there remained a dark-coloured substance which showed a metallic lustre under the file.

Metallic strontium in small fragments absorbs nitrogen directly. Absorption begins at 380° C. and is complete at 750° C., giving a black hygroscopic nitride which retains the form of the original metal.[13] It is decomposed by water with the formation of strontium hydroxide and ammonia. With carbon it forms a certain amount of strontium cyanide, but with carbon monoxide, strontium oxide, carbon, and nitrogen are chiefly formed.

Strontium Azide, $Sr(N_3)_2$, is formed by treating strontium oxide with a 2 per cent. solution of hydrazoic acid and crystallising over sulphuric acid, or by boiling an excess of freshly precipitated strontium

[1] Anthon, *J. prakt. Chem.*, 1836, [1], 9, 338; Zettnow, *Jahresber.*, 1867, 215; Lefort, *Ann. Chim. Phys.*, 1878, [5], 15, 321.

[2] Schultze, *Annalen*, 1863, 126, 49; Michel, *Bull. Soc. franç. Min.*, 1879, 2, 142.

[3] Zambonini, *Zeitsch. Kryst. Min.*, 1905, 41, 61.

[4] Lefort, *loc. cit.*

[5] Smith and Bradbury, *Ber.*, 1891, 24, 2930.

[6] Lotz, *Annalen*, 1854, 91, 61; *Ann. Chim. Phys.*, 1855, [3], 43, 246; Lefort, *loc. cit.*; *Ann. Chim. Phys.*, 1879, [5], 17, 477; von Knorre, *Ber.*, 1885, 18, 326; Scheibler, *J. prakt. Chem.*, 1860, [1], 80, 204; 1861, [1], 83, 273; Péchard, *Compt. rend.*, 1889, 108, 1167.

[7] Péchard, *ibid*, 1890, 110, 754.

[8] Klein, *Ann. Chim. Phys.*, 1883, [5], 28, 350.

[9] Gonzalez, *J. prakt. Chem.*, 1887, [2], 36, 55.

[10] Engels, *Zeitsch. anorg. Chem.*, 1903, 37, 125.

[11] Ditte, *Compt. rend.*, 1882, 95, 988.

[12] Maquenne, *ibid.*, 1892, 114, 25, 220; *Bull. Soc. chim.*, 1892, [3], 7, 366; *Ann. Chim. Phys.*, 1893, [6], 29, 225.

[13] Dafert and Miklauz, *Monatsh.*, 1913, 34, 1685.

hydroxide with a solution of ammonium azide.[1] Colourless, rhombic, hygroscopic crystals are obtained, which are isomorphous with the calcium and barium salts, and are exploded by heat but not by shock. The explosion temperature is 169° C.[2] The temperature at which evolution of nitrogen *in vacuo* begins is 140° C., and the reaction may then be continued at 110° C.[3]

It is readily soluble in water, 100 parts dissolving 45·83 parts of the salt at 16° C., and 100 of alcohol 0 095 parts. It is insoluble in ether.[4]

Strontium Ammonium, or Strontium Hexammoniate, $Sr(NH_3)_6$, is prepared by the action of dry ammonia on pure strontium cooled to $-60°$ C. Excess of ammonia produces a dark blue liquid, which, on evaporation *in vacuo*, gives off ammonia and deposits bronze-coloured crystals. The tension of dissociation is 42·2 mm. at 0° C. and 275 mm. at 33·5° C.[5] Oxygen acts upon a solution of the compound in ammonia at $-55°$ to $-40°$ C., with the formation of a mixture of oxide and peroxide.[6]

The heat of formation of strontium hexammoniate from the metal and ammonia is 9·90 Cal.[7]

Strontium Amide, $Sr(NH_2)_2$.—Strontium ammonium is decomposed under reduced pressure, slowly at 20° C. and rapidly above that temperature, evolving a mixture of ammonia and hydrogen, and leaving a white mass of strontium amide. When dry ammonia is passed over strontium heated to 200° C., hydrogen and nitrogen are obtained and some strontiamide. At 800° C. a mixture of hydride and nitride is formed.[6]

By the absorption of hydrogen by strontium nitride, Dafert and Miklauz obtained a compound to which they gave the formula $Sr_3(NH_2)_2$.[8] The reaction begins at 270°–280° C. and is very vigorous at 450° C. The product should be heated slowly to 600°–700° C. to complete the absorption.

Franklin obtained the compound, potassium ammonostrontianate, $SrNK.2NH_3$ or $Sr(NH_2)_2.KNH_2$, similar to potassium ammonocalciate.[9]

Strontium Imide, SrNH, is formed by the absorption of nitrogen by strontium hydride. The reaction begins at 500° C., and becomes vigorous at 850° C. At still higher temperatures there is partial formation of the nitride. The imide is an orange-yellow substance, becoming greenish-black when exposed to sunlight.[8]

Strontium Imidosulphonate, $Sr_3N_2(SO_3)_4$.—By mixing together solutions of strontium chloride and normal sodium imidosulphonate the strontium sodium salt, $SrNaNS_2O_6.3H_2O$, is formed.[10] The normal strontium salt can be obtained from this by dissolving in dilute hydrochloric acid, pouring at once into a slight excess of a warm concentrated

[1] Dennis and Benedict, *J. Amer. Chem. Soc.*, 1898, 20, 225 ; Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 286.
[2] Wöhler and Martin, *Zeitsch. angew. Chem.*, 1917, 30, 33.
[3] Tiede, *Ber.*, 1916, 49, 1742.
[4] Curtius and Rissom, *loc. cit.*
[5] Biltz and Hüttig, *Zeitsch. anorg. Chem.*, 1920, 114, 241 ; Biltz, *Zeitsch. Elektrochem.*, 1920, 26, 374 ; Roederer, *Compt. rend.*, 1905, 140, 1252.
[6] Roederer, *Bull. Soc. chim.*, 1906, [3], 35, 715.
[7] Biltz, *loc. cit.*
[8] Dafert and Miklauz, *loc. cit.*
[9] Franklin, *J. Amer. Chem. Soc.*, 1915, 37, 2295.
[10] Berglund, *Jahresber.*, 1876, 177.

solution of strontium hydroxide, and repeating twice to remove sodium. It forms thin glistening scales, and resembles the barium salt but is more soluble. The freshly dried salt contains 12 molecules of water, but after fourteen days' exposure only 5 molecules. By precipitating with a concentrated solution of the ammonium salt and evaporating in a desiccator, a hydrate containing 5 or $5\frac{1}{2}$ molecules of water of crystallisation is formed. By boiling the duodecahydrate a slightly basic pentahydrate is obtained.

Crystalline acid and basic salts have also been prepared,[1] and a mercurimidosulphonate, $HgSr_2N_2(SO_3)_4.15H_2O$.[2]

Strontium Hyponitrite, SrN_2O_2, is obtained by the action of strontium chloride on silver hyponitrite, and crystallises with 5 molecules of water, which it retains even at 100° C.[3] It is also formed when nitric oxide acts upon strontium ammonium dissolved in ammonia.[4]

With acetic acid it forms the compound $SrN_2O_2.Sr(CH_3COO)_2$. $2CH_3COOH.3H_2O$.[5]

Strontium Nitrohydroxylaminate, SrN_2O_3, is formed similarly to the calcium salt as a fine crystalline precipitate of composition $SrN_2O_3.1\frac{1}{2}H_2O$.[6] When dried at 100°–120° C. it corresponds to the formula $SrN_2O_3.H_2O$.[7]

Strontium Nitrite, $Sr(NO_2)_2$, is prepared similarly to the calcium salt by the action of silver nitrite on strontium chloride.[8] It has a yellow colour more pronounced than that of calcium nitrite, and crystallises at ordinary temperatures as the monohydrate of density 2·408.[9] By evaporation at 70°–80° C. the anhydrous salt is obtained.[10] It melts, and at the same time decomposes, at about 240° C.

The molecular volumes of the nitrides have been studied by Rây.[11]

Oswald has determined the solubility in water and obtained the following values[9] :—

Temperature, ° C. . .	0	20	40	60	80	100
Parts $Sr(NO_2)_2.H_2O$ per 100 parts water	58·9	75·5	94	116	145	182

The saturated solution boils at 112·5° C. under a pressure of 763 mm., and there is slow but decided hydrolysis. The cryohydric temperature is −6·8° C., and the composition of the solution 32·8 per cent. of nitrite.

A double salt with cæsium, $CsSr(NO_2)_3.H_2O$, and a triple salt with cæsium and silver, $Cs_3AgSr(NO_2)_6.2H_2O$, are known,[12] and also a double strontium mercury salt, $3Hg(NO_2)_2.2Sr(NO_2)_2.5H_2O$.[13]

Strontium Nitrate, $Sr(NO_3)_2$, may be obtained by dissolving strontium hydroxide or carbonate in nitric acid and crystallising from

[1] Divers and Haga, *Trans. Chem. Soc.*, 1896, **69**, 1622.
[2] Berglund, *Jahresber.*, 1876, 177.
[3] Kirschner, *Zeitsch. anorg. Chem.*, 1898, **16**, 426; but see Maquenne, *Ann. Chim. Phys.*, 1889, [6], **18**, 562.
[4] Roederer, *loc. cit.*
[5] Maquenne, *loc. cit.*
[6] Angeli and Angelico, *Gazzetta*, 1900, **30**, i, 593.
[7] Angelico and Fanara, *ibid.*, 1901, **31**, ii, 15.
[8] Vogel, *Zeitsch. anorg. Chem.*, 1903, **35**, 385; see also Hampe, *Annalen*, 1863, **125**, 340.
[9] Oswald, *Ann. Chim. Phys.*, 1914, [9], **1**, 32.
[10] Vogel, *loc. cit.*
[11] Rây, *Proc. Chem. Soc.*, 1908, **24**, 240; *Trans. Chem. Soc.*, 1909, **95**, 66.
[12] Jamieson, *Amer. Chem. J.*, 1907, **38**, 614.
[13] Rây, *Trans. Chem. Soc.*, 1910, **97**, 326.

the hot solution. It is prepared technically by precipitation from concentrated solutions of strontium chloride and sodium nitrate.[1] It forms octahedra or cubic octahedra isodimorphous with strontium chlorate[2] and of density 2·98 at 16·8° C.[3] Its melting-point is 645° C.[4] With potassium and sodium nitrates it forms a ternary eutectic mixture of melting-point 208·4° C., consisting of 9 equivalents of strontium, 50 of potassium, and 41 of sodium.[5]

From a cold saturated solution the tetrahydrate, $Sr(NO_3)_2.4H_2O$, separates out in monoclinic prisms[6] of density 2·11–2·25.[7] These melt in their water of crystallisation, which is readily lost at 100° C.[8] It has also been stated that a dihydrate separates from cold solutions.[9] It is probable that the transition temperature from the tetrahydrate to the anhydrous form is between 30° and 40° C., because at 32° C. both forms have been obtained by crystallisation from solution.[10] The heat of solution of the anhydrous salt is 4·62 Cal., and of the hydrated −3·05 Cal. The heat of hydration is 7·68 Cal.[11]

The following values for the solubility of strontium nitrate are compiled from various data[12] :—

Temperature, ° C.	−6	0	10	20	30	40	60	80	100	108
Parts $Sr(NO_3)_2$ in 100 parts water	32·5	39·5	59·0	68·0	87·6	91·3	94·0	97·2	101	103

The densities[13] and boiling-points,[14] the coefficients of expansion,[15] the freezing-points,[16] the viscosities,[17] the refractive indices,[18] and the equivalent conductivities[19] of solutions of different concentrations have been studied.

Strontium nitrate is not very soluble in alcohol, one part dissolving in 8500 of alcohol.[20] No compound is formed. The tetrahydrate is in equilibrium with solutions in dilute alcohol, but the anhydrous salt with solutions in concentrated alcohol.[21]

[1] Muck, Ber., 1883, 16, 2324.
[2] Traube, Zeitsch Kryst. Min., 1894, 23, 135.
[3] Clarke, Constants of Nature, Part I. (Macmillan & Co.), 1888, p. 111.
[4] Carnelley, Trans. Chem. Soc., 1878, 33, 279. A much lower value, 570° C., is given by Ramsay and Eumorfopoulos, Phil. Mag., 1896, [5], 41, 365.
[5] Harkins and Clarke, J. Amer. Chem. Soc, 1915, 37, 1816.
[6] Laurent, Ann. Chim. Phys., 1852, [3], 36, 352; Baker, Chem. News, 1880, 42, 196. According to de Sénarmont, Ann. Chim. Phys., 1854, [3], 41, 326, it contains $5H_2O$.
[7] Favre and Valson, Jahresber., 1873, 88.
[8] Souchay and Lenssen, Annalen, 1856, 99, 45.
[9] de Coppet, Ann. Chim. Phys., 1872, [4], 25, 547.
[10] Baker, loc. cit.; see also Findlay, Morgan, and Morris, Trans Chem. Soc, 1914, 105, 779.
[11] Thomsen, Thermochemistry, English translation by Burke (Longmans, Green & Co.), 1908, pp. 62, 86.
[12] Kremers, Pogg. Annalen, 1854, 92, 497; Etard, Ann. Chim. Phys., 1894, [7], 2, 528.
[13] Gerlach, Zeitsch. anal Chem., 1888, 27, 283, 329; Jones and Getman, Zeitsch. physikal. Chem., 1904, 49, 407.
[14] Gerlach, Zeitsch. anal. Chem., 1887, 26, 448; Smits, Zeitsch. physikal. Chem., 1902, 39, 418; Jones and Getman, loc. cit.
[15] Lannoy, Zeitsch. physikal. Chem., 1895, 18, 469.
[16] de Coppet, Ann. Chim. Phys., 1872, [4], 25, 548; Jones and Getman, loc. cit.
[17] Wagner, Wied. Annalen, 1883, 18, 259; Zeitsch. physikal. Chem., 1890, 5, 31.
[18] Jones and Getman, loc. cit.
[19] Kohlrausch and Grüneisen, Sitzungsber. K. Akad. Wiss. Berlin, 1904, 1215; Kahlenberg, J. Physical Chem., 1901, 5, 339; Jones and Getman, loc. cit.
[20] Rose, Pogg. Annalen, 1860, 110, 296.
[21] d'Ans and Siegler, Zeitsch. physikal. Chem., 1913, 82, 38.

Strontium nitrate dissolves to a considerable extent in liquid ammonia in which it is a good electrolyte.[1]

The solubilities of strontium nitrate and hydroxide in presence of each other have been studied at 25° C., but no basic salts have been isolated.[2]

Strontium nitrate is used in pyrotechnics for the production of red light.

STRONTIUM AND PHOSPHORUS.

Strontium Phosphide, Sr_3P_2, has been prepared by heating lamp-black with strontium phosphate in the electric furnace. It forms reddish-brown crystals of density 2·68, fusible in the electric arc. It burns in fluorine at room temperature, in chlorine at 30° C., in bromine vapour at 175° C., in iodine vapour at red heat, in oxygen at 300° C., and in sulphur at a still higher temperature. It is decomposed by carbon at a high temperature but not by sodium at red heat, by dilute acids and gaseous acids but not by concentrated acids, sulphuretted hydrogen, ammonia, nor organic solvents. It changes rapidly in moist air, and is decomposed by water with the liberation of phosphoretted hydrogen. Oxidising agents attack it violently.[3]

Strontium Dihydrohypophosphite, $Sr(H_2PO_2)_2$, is formed by the action of phosphorus on strontium sulphide or on a boiling solution of strontium hydroxide, or by dissolving strontium carbonate in hypophosphorous acid. It forms stable anhydrous leaflets, soluble in water but not in alcohol.[1] On heating, it breaks up similarly to the calcium salt into water, phosphoretted hydrogen, and the pyro- and meta-phosphates,[5] the two latter being in the molecular proportions of 3 to 1.[6]

Strontium Hydrophosphite, $SrHPO_3.H_2O$, or $H_4Sr_2P_2O_7.2H_2O$, is obtained as a crystalline precipitate, not readily soluble in water, by the interaction of ammonium phosphite with strontium chloride.[7] It loses water at 200° C.[7] On boiling with water a basic salt is formed, and after calcination strontium pyrophosphate is left.[8]

Strontium Dihydrophosphite, $SrH_4P_2O_6$, is obtained by dissolving strontium carbonate in phosphorous acid in the proportions of one molecule of the former to two of the latter.[9] It forms small crystals which are unaffected by heating to 100° C. By dehydration the pyrophosphite, $SrH_2P_2O_5$, is obtained.[10]

Strontium Orthophosphates.—*Tristrontium Phosphate, $Sr_3P_2O_8$,* is obtained by the precipitation of strontium chloride with sodium phosphate in ammoniacal solution. It first separates in the colloidal state[11] with absorption of heat, but it then slowly crystallises with the evolution of heat.[12] When dried at 100° C. it forms a hard vitreous

[1] Franklin and Kraus, *Amer. Chem. J.*, 1900, **23**, 301.
[2] Parsons and Perkins, *J. Amer. Chem. Soc.*, 1910, **32**, 1387.
[3] Jaboin, *Compt. rend.*, 1899, **129**, 762.
[4] Wurtz, *Ann. Chim. Phys.*, 1846, [3], **16**, 194.
[5] Rose, *Pogg. Annalen*, 1827, **9**, 372.
[6] Rammelsberg, *Ber.*, 1872, **5**, 492.
[7] Rammelsberg, *Pogg. Annalen*, 1867, **131**, 273.
[8] Rammelsberg, *loc. cit.* ; Rose, *Pogg. Annalen*, 1827, **9**, 27.
[9] Amat, *Ann. Chim. Phys.*, 1891, [6], **24**, 312.
[10] Amat, *ibid.*, p. 354.
[11] Barthe, *Compt. rend.*, 1892, **114**, 1267.
[12] Berthelot, *ibid.*, 1886, **103**, 911.

substance. It is insoluble in water and is decomposed by boiling water, but it is soluble in phosphoric acid forming monostrontium orthophosphate.

Halogen compounds of tristrontium phosphate, of the type $3Sr_3P_2O_8.SrF_2$, corresponding to the calcium apatites, are known.[1]

Distrontium Phosphate, $SrHPO_4$, is formed as a gelatinous precipitate by adding a slightly acid solution of strontium chloride to disodium hydrogen phosphate below 50° C. It gradually crystallises with 2 molecules of water.[2] It is insoluble in water but soluble in acids and in some salt solutions. There is also an anhydrous salt, strontium monetite, of density 3·544.[3]

Monostrontium Phosphate, $SrH_4(PO_4)_2.2H_2O$, is obtained by the action of dilute phosphoric acid on strontium hydroxide, or on distrontium phosphate, under suitable temperature conditions.[4]

With regard to the study of the solubility of the three strontium orthophosphates, owing to their decomposition by water, the same difficulties arise as in the case of the calcium compounds.

Strontium Pyrophosphate, $Sr_2P_2O_7$, can be formed by heating distrontium orthophosphate alone, or sodium meta- or pyro-phosphate with strontium oxide, or strontium sulphate with potassium pyrophosphate,[5] or by the precipitation of strontium nitrate with sodium pyrophosphate.[6] The density of the anhydrous salt at 20° C. is 3·4.

Prepared in the wet way it crystallises with 1 molecule of water. It is soluble in acids, but only slightly soluble in water. Pahl obtained a hydrate with $2\frac{1}{2}$ molecules of water as well as a number of acid pyrophosphates, all of which are infusible at red heat.[7]

Strontium Metaphosphate, $Sr(PO_3)_2$, is obtained by dissolving strontium carbonate in excess of phosphoric acid, evaporating, and heating.[8]

Strontium hexa-metaphosphate, $Sr_3P_6O_{18}$, is formed as a thick white flocculent precipitate by the action of the corresponding sodium salt on excess of strontium nitrate. When dried it forms an amorphous white powder, which is almost insoluble in water and melts to a glass if heated.[9]

Double Salts. — The following double phosphates have been described: the orthophosphates, $SrKPO_4$, $SrNaPO_4$, and $SrNaPO_4.9H_2O$; [10] the pyrophosphates, $SrK_2P_2O_7$ and $SrNa_2P_2O_7$;[11] and the metaphosphate, $NaSr(PO_3)_3.3H_2O$.[12] Colani mentions the compounds $ThO_2.SrO.P_2O_5$ [13] and $UO_2.SrO.P_2O_5$.[14]

[1] von Woyczynski, *Zeitsch. anorg. Chem.*, 1894, **6**, 310; Deville and Caron, *Ann. Chim. Phys.*, 1863, [3], **67**, 452; Ditte, *ibid.*, 1886, [6], **8**, 502; Winter, *Dissertation*, Leipzig, 1913, 1, see *J. Chem. Soc.*, 1914, **106**, Abs. ii, 126.

[2] Barthe, *loc. cit.*; Joly, *Compt. rend.*, 1886, **103**, 1197.

[3] de Schulten, *Bull. Soc. franç. Min.*, 1904, **27**, 109.

[4] Barthe, *loc. cit.*

[5] Ouvrard, *Compt. rend.*, 1888, **106**, 1599; *Ann. Chim. Phys.*, 1889, [6], **16**, 300.

[6] Schwarzenberg, *Annalen*, 1848, **65**, 144.

[7] Pahl, *Arkiv. Chem. Min. Geol.*, 1905, **2**, i, No. 6, 1, see *J. Chem. Soc.*, 1906, **90**, Abs. ii, 87.

[8] Maddrell, *Annalen*, 1847, **61**, 61.

[9] Lüdert, *Zeitsch. anorg. Chem.*, 1894, **5**, 35.

[10] Rose, *Pogg. Annalen*, 1849, **77**, 293; Joly, *Compt. rend.*, 1887, **104**, 905, 1702; Ouvrard, *ibid.*, 1888, **106**, 1599; *Ann. Chim. Phys.*, 1889, [6], **16**, 300.

[11] Baer, *Pogg. Annalen*, 1848, **75**, 166; Ouvrard, *loc. cit.*

[12] Lindbom, *Ber.*, 1875, **8**, 122.

[13] Colani, *Compt. rend.*, 1909, **149**, 207.

[14] Colani, *Ann. Chim. Phys.*, 1907, [8], **12**, 139.

Basic Strontium Phosphate, $4SrO.P_2O_5$, is obtained in small quadratic plates by fusion of excess of strontium oxide with sodium carbonate and neutral sodium phosphate.[1]

Strontium Thiophosphate.—The compound $Sr_3H_6(PS_3O)_4.aq.$ has been isolated.[2]

STRONTIUM AND ARSENIC.

Strontium Arsenide, Sr_3As_2, is prepared by the reduction of strontium arsenate by carbon in the electric furnace.[3] It is very similar in appearance to calcium arsenide, forming a transparent crystalline mass, reddish-brown in thin sections, and of density 3·6 at 15° C. Fluorine reacts in the cold with incandescence, producing white fumes of arsenic fluoride. Chlorine reacts at 160° C., bromine above 200° C., and iodine vapour when strongly heated. The arsenide burns in oxygen and in sulphur vapour above a low red heat. Carbon decomposes it in the electric furnace, giving carbide. It reacts with water in the cold.

Strontium Orthoarsenites.—An impure tristrontium orthoarsenite, containing more strontium than corresponds to the formula $Sr_3As_2O_6$, has been obtained as a white flocculent precipitate by treating strontium chloride solution with potassium orthoarsenite in the cold.[4] The distrontium orthoarsenite, $SrHAsO_3.H_2O$, may also be obtained by first precipitating the amorphous arsenite by the action of an alkali arsenite on a strontium salt, dissolving in acetic acid, and evaporating the solution.[1]

Strontium Pyroarsenite, $Sr_2As_2O_5.2H_2O$, may be prepared by adding an aqueous arsenious acid solution to strontium chloride dissolved in alcohol, leaving to stand for some time, and drying the white flocculent precipitate at 100° C. It is easily soluble in water and in acids.[4]

Strontium Metarsenite, $Sr(AsO_2)_2.4H_2O$, has been prepared by the action of ammonium arsenite on a solution of a strontium salt. The precipitate is increased by the addition of alcohol, since it is fairly soluble in water. When dried at 100° C. it has the composition $Sr(AsO_2)_2.3H_2O$. At higher temperatures it is decomposed.[5] Stavenhagen failed to obtain this compound.

Strontium Orthoarsenates.—By fusing sodium arsenate with strontium oxide and alkali chlorides, tristrontium arsenate in long colourless orthorhombic prisms is obtained, provided the proportion of arsenate is not below 12 per cent. of the mixture when chlorinated products are formed. It is soluble in dilute acids but not affected by boiling water.[6] It may also be prepared by adding strontium hydroxide solution to arsenic acid and washing the precipitate to neutrality.[7]

Compounds with strontium halides corresponding to apatite and wagnerite have been prepared.[8]

Distrontium orthoarsenate, $SrHAsO_4$, is obtained as a crystalline precipitate from hot solutions of disodium arsenate and strontium

[1] von Woyczynski, Zeitsch. anorg. Chem., 1894, 6, 310. See Basic Calcium Phosphate.
[2] Ephraim and Stein, Ber., 1911, 44, 3405.
[3] Lebeau, Compt. rend., 1899, 129, 47 ; Ann. Chim. Phys., 1902, [7], 25, 470.
[4] Stavenhagen, J. prakt. Chem., 1895, [2], 51, 16.
[5] Stein, Annalen, 1850, 74, 218.
[6] Lefèvre, Ann. Chim. Phys., 1892, [6], 27, 19 ; Ditte, ibid., 1886, [6], 8, 502.
[7] Blarez, Compt. rend., 1886, 103, 639.
[8] Lefèvre, loc. cit. ; Ditte, loc. cit. ; Compt. rend., 1883, 96, 846, 1226 ; von Woyczynski, Zeitsch. anorg. Chem., 1894, 6, 310.

chloride.   When dried at 100° C. it has the formula $Sr_2H_2(AsO_4)_2.3H_2O$.[1]
It is soluble in acetic acid and crystallises out in leaflets as $SrHAsO_4.H_2O$,[2]
strontium haidingerite, of density 3·606 at 15° C.[3]   The anhydrous salt,
strontium arsenomonetite, forms triclinic prisms of density 4·035.[4]

Several double arsenates with the alkalies are formed, $SrNaAsO_4$,
$SrKAsO_4$,[5] $SrNaAsO_4.18H_2O$,[6] $SrNaAsO_4.H_2O$, and $9H_2O$.[7]

Strontium Pyroarsenate, $Sr_2As_2O_7$, is formed as colourless
transparent crystals by the action of fused potassium metarsenate on
strontium oxide and subsequent treatment with anhydrous glycerol.[8]
Chloride may be substituted for the oxide provided that the arsenate
forms more than 70 per cent. of the mixture.[5]   The salt is hydrated by
the action of cold water.

Strontium Thioarsenites.—Two thioarsenites, $2(SrS.As_2S_3).5H_2O$
and $2SrS.As_2S_3.15H_2O$, have been obtained by the action of thioarsenious
acid on strontium sulphide in aqueous solution.[9]

Strontium Thio-oxyarsenates.—The compounds $Sr_2Na_2As_2O_6S_2$.
$17H_2O$ [10] and $NaSrAsOS_3.10H_2O$ [11] have been separated.

STRONTIUM AND ANTIMONY.

Strontium Thioantimonite.—By the action of strontium sulphide
in aqueous solution on antimony sulphide, a white crystalline ortho-
thioantimonite, $Sr_3Sb_2S_6.10H_2O$, and a yellow crystalline pyrothioanti-
monite, $Sr_2Sb_2S_5.15H_2O$, are formed.[12]

Strontium Antimonate, $SrSb_2O_6.xH_2O$, is formed as a white
amorphous precipitate by the action of sodium antimonate on strontium
chloride.[13]

STRONTIUM AND VANADIUM.

Strontium Orthovanadate, $Sr_3(VO_4)_2$, has been obtained as
transparent yellowish leaves by heating vanadic acid with sodium
and strontium iodides.[14]   Halogen compounds corresponding to the
apatites and wagnerites have also been obtained.[15]

Strontium Metavanadate, $SrV_2O_6.4H_2O$, is prepared as a faintly
yellow, powdery precipitate by the action of the normal potassium salt
on strontium chloride.[16]   It loses 2 molecules of water over sulphuric
acid, and the rest at 280° C., when it melts to a brown glass.

A number of acid salts have been obtained, which, on treatment

[1] Kotschoubey, *Annalen*, 1850, 76, 249.
[2] Schiefer, *Jahresber.*, 1864, 237.
[3] de Schulten, *Bull. Soc. franç. Min.*, 1904, 27, 104.
[4] de Schulten, *ibid.*, p. 109.
[5] Lefèvre, *loc. cit.*
[6] Joly, *Compt. rend.*, 1887, 104, 905, 1702.
[7] Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 129.
[8] Lefèvre, *Compt. rend.*, 1889, 108, 1058.
[9] Nilson, *J. prakt. Chem.*, 1876, [2], 14, 52.
[10] McCay, *Chem. Zeit.*, 1897, 21, 487.
[11] McCay and Foster, *Zeitsch. anorg. Chem.*, 1904, 41, 462.
[12] Pouget, *Compt. rend.*, 1898, 126, 1792.
[13] Heffter, *Pogg. Annalen*, 1852, 86, 418.
[14] Ditte, *Compt. rend.*, 1883, 96, 1048 ; *Ann. Chim. Phys.*, 1886, [6], 8, 502.
[15] Ditte, *Compt. rend.*, 1883, 96, 846, 1226 ; *Ann. Chim. Phys.*, 1886, [6], 8, 502.
[16] Berzelius, *Pogg. Annalen*, 1831, 22, 57 ; Manasse, *Annalen*, 1887, 240, 23.

with water, give the normal salt.[1] There are also some double strontium potassium acid salts.[2]

Strontium Pervanadate, $Sr(VO_4)_2$, is obtained as a yellow flocculent precipitate by mixing together strontium chloride and a saturated ammonium pervanadate solution, washing with hydrogen peroxide, and drying over calcium chloride.[3]

STRONTIUM AND CARBON.

Strontium Carbide, SrC_2, may be obtained by the action of sugar charcoal on strontium oxide or strontium carbonate in the electric furnace. It forms a black mass with a brown-red crystalline fracture, and has a density of 3·19. It decomposes water with the formation of acetylene, and, in general, its chemical behaviour is similar to that of calcium carbide, but it is somewhat more reactive.[4] When heated strongly in the electric furnace, strontium carbide will dissolve as much as 6 per cent. of carbon.[5]

Strontium Carbonyl, $Sr(CO)_2$.—When a solution of strontium ammonium in ammonia is treated with carbon monoxide at −45° C., a dull yellow, powdery mass of strontium carbonyl is obtained. It becomes bright yellow on exposure to moist air, forms a clear yellow solution with water, and blackens when heated under reduced pressure yielding a mixture of carbon with strontium oxide and carbonate.[6]

Strontium Formate, $Sr(HCO_2)_2$, is formed in solution by neutralising formic acid with strontium oxide or carbonate. From this solution a dihydrate of density 2·667 [7] crystallises out below about 83° C.,[8] and above that temperature the anhydrous salt of density 2·250.[7]

The dihydrate exists in two different rhombic crystalline forms.[9]

The freezing-point lowering of water produced by strontium formate has been determined.[10] The molecular refractivity is 49·01.[11]

A double strontium copper formate, $2Sr(HCO_2)_2.Cu(HCO_2)_2.2H_2O$, of density 2·133, has been prepared.[7]

Strontium Acetate, $Sr(C_2H_3O_2)_2$, crystallises in the cold with 4 molecules of water, and at 15° C. with 0·5 molecule. It is readily soluble in water, but not in alcohol. The value of the electrolytic dissociation as determined from the freezing-point lowering [10] is much greater than that given by electrical conductivity methods.[12]

Acid salts have also been obtained.[13]

[1] Manasse, *loc. cit.* ; von Hauer, *Jahresber.*, 1859, 177 ; *J. prakt. Chem.*, 1856, [1], 69, 401 ; Norblad, *Ber.*, 1875, 8, 126 ; Scheuer, *Zeitsch. anorg. Chem.*, 1898, 16, 284.

[2] Manasse, *loc. cit.*

[3] Scheuer, *loc. cit.*

[4] Moissan, *Compt. rend.*, 1894, 118, 683 ; *The Electric Furnace*, English translation (Williams & Norgate), 1908 ; see also Kahn, *Compt. rend.*, 1907, 144, 913.

[5] Kahn, *ibid.*, 1907, 144, 197.

[6] Roederer, *Bull. Soc. chim.*, 1906, [3], 35, 715.

[7] Schröder, *Ber.*, 1881, 14, 21.

[8] Stanley, *Chem. News*, 1904, 89, 193 ; see also Plathan, *J. Chem. Soc.*, 1899, 76, Abs. i, 253.

[9] Pasteur, *Ann. Chim. Phys.*, 1851, [3], 31, 98.

[10] Calame, *Zeitsch. physikal. Chem.*, 1898, 27, 401.

[11] Kanonnikoff, *J. prakt. Chem.*, 1885, [2], 31, 321.

[12] MacGregory, *Wied. Annalen*, 1894, 51, 126.

[13] Villiers, *Compt. rend.*, 1877, 84, 774.

Strontium Oxalate, SrC_2O_4, may be obtained as the monohydrate by precipitation from a concentrated solution of strontium chloride by ammonium oxalate.[1]   At low temperatures it crystallises with $2\frac{1}{2}$ molecules of water.   The solubility of strontium oxalate at 18° C., as calculated from electrical conductivity determinations, is 0·26 millimole, or 46·1 mgm. of anhydrous salt per litre.[2]   A small quantity of acetic acid increases the solubility of strontium oxalate, which reaches a maximum in approximately $4N$ acid.   By higher concentrations the solubility is again diminished.[3]

Strontium Carbonate, $SrCO_3$, occurs in nature as the mineral *strontianite*, of density 3·4–3·7, and isomorphous with aragonite.   It may be formed by precipitation from strontium chloride solution by ammonium carbonate, or by the action of carbon dioxide on heated strontium hydroxide,[4] or strontium oxide at red heat.[5]

For the technical production several methods may be employed :—

1. Fusion of celestine with sodium carbonate.[6]

2. Boiling celestine with a concentrated solution of ammonium carbonate.[7]

3. Action of a mixture of calcium chloride, carbon, and metallic iron on celestine at red heat.   The sulphate is thus converted into the carbonate by ammonium carbonate, or by milk of lime and carbon dioxide.[8]

4. Boiling with magnesium chloride a solution of strontium hydrosulphide through which carbon dioxide is passing.[9]

The precipitated carbonate can be transformed into strontianite by crystallisation from solution in fused alkali chlorides.[10]

The specific heat of strontianite is 0·1445,[11] and of the precipitated carbonate 0·14483.[12]   The density of the precipitated carbonate is 3·55–3·62.[13]

Strontium carbonate is less readily decomposed by heat than calcium carbonate.   Its dissociation pressure reaches 1 atmosphere of carbon dioxide at about 1155° C.,[14] but the rate of decomposition only becomes rapid when a temperature of 1255° C. is reached.[15]

The heat of formation of crystallised strontium carbonate from strontium oxide and carbon dioxide is 57·3 Cal.[16]

Strontium carbonate is dimorphic, the transition point to the α-form being 920°–929° C.[17]   α-Strontium carbonate belongs to the hexagonal

[1] Kohlrausch, *Zeitsch. physikal. Chem*, 1908, **64**, 129.

[2] Kohlrausch, *loc. cit.* ; *Zeitsch. physikal. Chem.*, 1904, **50**, 355;   Kohlrausch and Rose, *ibid*, 1893, **12**, 234.

[3] Herz and Muhs, *Ber.*, 1903, **36**, 3715.

[4] Scheibler, *ibid.*, 1886, **19**, 1973.

[5] Raoult, *Compt. rend.*, 1881, **92**, 1110.

[6] Urquhart and Rowell, *Dingl. poly. J.*, 1884, **252**, 332.

[7] Mebus and Decastro, *ibid.*, 1885, **257**, 198.

[8] Lieber, *ibid.*, 1883, **250**, 69 ; German Patent, 22364 (1882).

[9] Claus, *Dingl. poly. J.*, 1884, **253**, 83 ; Schaibler, *loc. cit.*

[10] Bourgeois, *Ann. Chim. Phys.*, 1883, [5], **29**, 486.

[11] See Kopp, *Annalen Suppl.*, 1864–5, **3**, 295.

[12] Regnault, *Ann. Chim. Phys.*, 1841, [3], **1**, 182.

[13] Schröder, *Jahresber.*, 1859, 12.

[14] Brill, *Zeitsch. anorg. Chem*, 1905, **45**, 281 ; Johnston, *J. Amer. Chem. Soc.*, 1908 **30**, 1357 ; see also Conroy, *J. Soc. Chem. Ind.*, 1891, **10**, 104 ; de Forcrand, *Compt. rend.*, 1908, **146**, 511.

[15] Hedvall, *Zeitsch. anorg. Chem.*, 1916, **98**, 52.

[16] de Forcrand, *loc. cit.*

[17] Boeke, *Chem. Zentr.*, 1913, i, 1909.

system. The melting-point in an atmosphere of carbon dioxide under pressure is 1497° C.[1]

Strontium carbonate is only very slightly soluble in water, the solubility at 18° C. being 11 mgm. per litre,[2] and the solubility product $[Sr^{++}] \times [CO_3^{--}] = 1 \cdot 567 \times 10^{-9}$.[3] This value was deduced from experiments carried out under a pressure of carbon dioxide varying from 0·05–1·1 atmosphere. A saturated solution of strontium carbonate under ordinary atmospheric conditions reacts alkaline, owing to hydrolysis. The solubility is increased by the presence of carbon dioxide in the water, through the formation of the acid carbonate in solution. It is also increased by the presence of ammonium chloride or nitrate.

A colloidal solution of strontium carbonate may be formed by passing carbon dioxide through a methyl alcoholic solution of strontium oxide. No separation of the gel takes place.[4]

By the addition of a solution of strontium chloride to a saturated solution of potassium carbonate a transparent jelly-like mass, consisting of the double salt, $SrCO_3.K_2CO_3$, is obtained, and this, on stirring, becomes opaque and finally granular.[5]

The crystalline double salts, $SrCO_3.K_2CO_3$ and $SrCO_3.Na_2CO_3$, may be prepared by fusion.[6]

Strontium Trithiocarbonate, $SrCS_3.4H_2O$, is obtained in the form of dark red needles by the action of carbon disulphide on strontium hydrosulphide in alcoholic solution and precipitation by ether. These become yellow on drying *in vacuo* and are much more soluble than the barium salt or the basic calcium salts.[7]

Strontium Perthiocarbonate, $SrCS_4.8H_2O$.—By substituting the disulphide for the hydrosulphide in the previous reaction, Yeoman obtained the perthiocarbonate as yellow crystals. It forms a yellow aqueous solution which can dissolve no more sulphur. It is soluble in alcohol, and is reprecipitated by ether as a red oil.

Strontium Cyanide, $Sr(CN)_2$, may be formed by the absorption of nitrogen by strontium carbide,[8] or, in very small quantity, by the action of carbon monoxide on the nitride at red heat.[9] By passing anhydrous hydrocyanic acid over crystallised strontium hydroxide, a solution of strontium cyanide in the water of crystallisation of the hydroxide is obtained. It is unstable in the presence of excess of hydrocyanic acid. On evaporation *in vacuo* deliquescent orthorhombic crystals of the tetrahydrate, $Sr(CN)_2.4H_2O$,[10] separate out. If dehydration of the crystals *in vacuo* is attempted they lose hydrocyanic acid as well as

[1] Boeke, *Chem. Zentr.*, 1913, i, 1909.

[2] Kohlrausch and Rose, *Zeitsch. physikal. Chem.*, 1893, **12**, 241 ; see also Bineau, *Ann. Chim. Phys.*, 1857, [3], **51**, 299.

[3] McCoy and Smith, *J. Amer. Chem. Soc.*, 1911, **33**, 468. See also Calcium Carbonate.

[4] Neuberg and Rewald, *Biochem. Zeitsch.*, 1908, **9**, 540.

[5] Datta and Mukherjea, *Proc. Chem. Soc.*, 1913, **29**, 185 ; but see Barro, *Compt. rend.*, 1912, **154**, 279.

[6] Le Chatelier, *ibid.*, 1894, **118**, 415.

[7] Yeoman, *Trans. Chem. Soc.*, 1921, **119**, 49; see Calcium Trithiocarbonate. See also Berzelius, *Pogg. Annalen*, 1826, **6**, 444.

[8] Tucker and Yang, *8th Inter. Cong. Appl. Chem.*, 1912, **21**, 121 ; *J. Chem. Soc.*, 1913, **104**, Abs. ii, 776.

[9] Maquenne, *Bull. Soc. chim.*, 1892, [3], **7**, 366.

[10] Mentzendorff, *Pogg. Annalen*, 1842, **56**, 70, described a trihydrate, $Sr(CN)_2.3H_2O$.

water.[1]   A solution can also be prepared by fusing strontium ferro-cyanide and extracting with water.[2]

Several double cyanides are known, some of them no doubt containing complex ions.   There is the strontium mercury compound, $SrHg(CN)_4.5H_2O$,[3] and also the compound $Sr(CN)_2.Hg(CN)_2.HgI_2.7H_2O$.[4] Strontium manganocyanide, $Sr_2Mn(CN)_6$, has been obtained, and strontium manganese manganocyanide, $SrMnMn(CN)_6$.[5]   There are also a cobaltocyanide and an unstable chromocyanide.[5]

Strontium Cyanamide, $SrCN_2$.—Strontium carbide absorbs nitrogen when heated to 1000°–1200° C. in an atmosphere of that gas, and, as happens in the case of barium, a mixture of cyanide and cyanamide is produced.[6]

If carbon dioxide is passed through an aqueous strontium cyanamide solution—obtained by dissolving strontium hydroxide crystals in aqueous cyanamide solution, filtering, and adding still more cyanamide—a crystalline powder of composition $4(SrCN_2.CO_2).9H_2O$ is precipitated.[7] It is less soluble in water than the corresponding calcium compound, and is rapidly decomposed in solution.

Strontium Thiocyanate, $Sr(CNS)_2.3H_2O$, may be prepared by boiling a solution of ammonium thiocyanate with strontium hydroxide until no more ammonia is given off, passing carbon dioxide through the liquid to remove excess of hydroxide, filtering, and evaporating.[8]   It is also formed by the action of thiocyanic acid on strontium carbonate.[9] It is a very deliquescent salt, easily soluble in water and alcohol.

A double salt is known, $2Hg(CN)_2.Sr(SCN)_2.4H_2O$, which loses 2 molecules of water on exposure to the air.[10]

Strontium Selenocyanate has been obtained as a crystalline salt of unknown composition.[9]   It forms well-defined prisms.[11]

STRONTIUM AND SILICON.

Strontium Silicide, $SrSi_2$, has been obtained by the reduction of a mixture of strontium oxide and silica by means of carbon in the electric furnace.[12]   It may also be prepared by heating together silicon and strontium oxide in an ordinary furnace.[13]

It is a white or bluish-white compound of metallic appearance, possessing a crystalline fracture and oxidising slowly in the air to silica and strontium oxide.   It is decomposed by water with the formation of strontium hydroxide, silica, and hydrogen.[14]

[1] Joannis, *Ann. Chim. Phys.*, 1882, [5], **26**, 482.
[2] Schulz, *J. prakt. Chem.*, 1856, [1], **68**, 257.
[3] Grossman and von Forst, *Ber.*, 1904, **37**, 4141.
[4] Varet, *Compt. rend.*, 1895, **121**, 499.
[5] Descamps, *Ann. Chim. Phys.*, 1881, [5], **24**, 178   For strontium platinocyanide and ferro- and ferri-cyanides, see Vol. IX. of this series, Parts I. and II.   See also Williams, *Cyanogen Compounds* (Churchill), 1915.
[6] Tucker and Yang, 8th *Inter. Cong. Appl. Chem.*, 1912, **21**, 121 ; *J. Chem. Soc.*, 1913, **104**, Abs ii, 776.
[7] Meyer, *J. prakt. Chem.*, 1878, [2], **18**, 419.
[8] Williams, *Cyanogen Compounds* (Churchill), 1915, p. 212.
[9] Meitzendorff, *Pogg. Annalen*, 1842, **56**, 70.
[10] Clève, *Bull. Soc. chim.*, 1875, [2], **23**, 71.
[11] Crookes, *J. Chem. Soc.*, 1852, **4**, 19.
[12] Bradley, *Chem. News*, 1900, **82**, 149 ; Mills, English Patent, 14124 (1900).
[13] Goldschmidt, German Patent, 199193, see *J. Chem. Soc.*, 1908, **94**, Abs. ii, 1037.
[14] Mills, *loc. cit.*

Strontium Silicate occurs naturally associated with barium and calcium as the silicoaluminate *brewsterite*, $H_4[Ba,Sr,Ca]Al_2Si_6O_{18}.3H_2O$. A metasilicate, in colourless, transparent, fibrous crystals, of density 3·652, has been formed by fusing a mixture of silica with strontium chloride and strontium carbonate.[1]   By rapid cooling, a practically isotropic glass of density 3·540 is obtained, but this can be transformed into the microcrystalline variety by careful heating.[2]   The heat of formation of strontium metasilicate from strontium oxide and silica is 21·3 Cal.[3]   Its melting-point is 1580° ±4° C.[4]   There is also an ortho-silicate melting above 1750° C.[2]

By the action of sodium metasilicate on a strontium salt a hydrated metasilicate, $SrSiO_3.H_2O$, is formed.[5]   Strontium hydroxide solution reacts with silicic acid or powdered quartz to produce a number of acid salts.[6]

Strontium Fluosilicate, $SrSiF_6$, is prepared by evaporating to dryness a solution of strontium carbonate in excess of hydrofluosilicic acid, treating with water, filtering to remove silica, and allowing to crystallise.[7]   It forms monoclinic crystals [8] of composition $SrSiF_6.2H_2O$, and density 2·99 at 17·5° C., which, on being heated, give first water and then silicon fluoride.   It is decomposed by water and by all acids except dilute hydrofluosilicic acid.[7]

One part of the salt dissolves in 31 parts of water at 15° C., and in 1529 parts of 50 per cent. alcohol.[9]

STRONTIUM AND TIN.

Strontium Stannate.—By the addition of potassium stannate to a solution of a strontium salt, or of strontium hydroxide, small transparent rhombohedra are obtained of composition $3SrO.2SnO_2.10H_2O$.   The compound is insoluble in water, but soluble in cold hydrochloric or nitric acid, forming a clear solution which gelatinises on heating.[10]

Chlorostannates, $SrSnCl_6.8H_2O$, $5H_2O$, and $4H_2O$,[11] a bromostan-nate, $SrSnBr_6.6H_2O$,[12] and a thiostannate, $SrSnS_3.12H_2O$,[13] have also been described.

STRONTIUM AND LEAD.

Strontium Orthoplumbate.—By heating together strontium car-bonate and lead oxide in air, a chocolate-coloured compound, probably of composition Sr_2PbO_4, is formed.   It is insoluble in water, but is slowly decomposed by it and also by acids.[14]

[1] Bourgeois, *Ann. Chim. Phys.*, 1883, [5], 29, 444.
[2] Jäger and van Klooster, *Sprechsaal*, 1919, 52, 256, see *J. Soc. Glass Tech.*, 1919, 3, 234A.
[3] Le Chatelier, *La Silice et les Silicates* (Hermann et Fils), 1914, p 52.
[4] Eskola, *Amer. J Sci.*, 1922, [5], 4, 331.
[5] Jordis and Kanter, *Zeitsch. anorg. Chem.*, 1903, 35, 82.
[6] Jordis and Kanter, *ibid.*, 1903, 35, 148 ; 1904, 42, 418 ; 1905, 43, 314.
[7] Stolba, *Chem. Zentr.*, 1880, 259
[8] Marignac, *Ann. Mines*, 1859, [5], 15, 221.
[9] Fresenius, *Zeitsch. anal. Chem.*, 1890, 29, 147.
[10] Ditte, *Compt. rend.*, 1883, 96, 701.
[11] Biron, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 489 ; Lewy, *Ann. Chim. Phys.*, 1846, [3], 16, 306 ; Poggiale, *Compt. rend.*, 1845, 20, 1183.
[12] Preis and Rayman, *Chem. Zentr.*, 1882, 773.
[13] Ditte, *Compt. rend.*, 1882, 95, 641.
[14] Kassner, *Arch. Pharm.*, 1890, 28, 109.

STRONTIUM AND TITANIUM.

Strontium Titanate.—By fusing together equivalent quantities of strontium carbonate and titanic acid with excess of strontium chloride the compound $2SrO.3TiO_2$ is formed as microscopic, light brown, cubic crystals of density $5\cdot1$.[1]

Strontium fluotitanate, $SrTiF_6.2H_2O$, isomorphous with the fluosilicate, has also been obtained.[2]

STRONTIUM AND ZIRCONIUM.

Strontium Zirconate, $SrZrO_3$, has been obtained by fusing zirconia with strontium oxide[3] or strontium chloride.[4] It is similar to the corresponding calcium compound.

STRONTIUM AND BORON.

Strontium Boride, SrB_6, is prepared by heating in the electric furnace a mixture of strontium borate, aluminium, and carbon. The impurities can be readily removed by flotation in bromoform on account of the density of strontium boride.[5] It forms a black crystalline powder, but, when in sufficiently thin layers, it is transparent with a reddish-brown coloration under the microscope. It is harder than quartz, and has a density of $3\cdot28$ at $15°$ C. Its chemical properties are similar to those of calcium boride, but it is slightly less reactive—for example, it is necessary to heat gently in fluorine in order to start the reaction.

Strontium Borates.—By following the freezing-point curve of mixtures of strontium oxide with boric anhydride, Guertler[6] established the existence of the pyroborate, $2SrO.B_2O_3$, the metaborate, $SrO.B_2O_3$,[7] the biborate, $SrO.2B_2O_3$, comparable with borax,[8] and possibly the orthoborate, $3SrO.B_2O_3$.[9] The metaborate crystallises in long, doubly refracting needles, and the pyroborate forms a finely crystalline, marble-like mass. Certain products formerly supposed to be compounds, for example $2SrO.3B_2O_3$ and $3SrO.2B_2O_3$, are probably only eutectic mixtures.

Compounds of varying composition and containing water of crystallisation are obtained by precipitation or by the action of boric acid on strontium hydroxide.[10] A strontium metaborate tetrahydrate, $SrO.B_2O_3.4H_2O$, has been obtained electrolytically.[11]

[1] Bourgeois, *Compt. rend.*, 1886, **103**, 141 : *Bull. Soc. chim.*, 1886, [2], **46**, 262.
[2] Marignac, *Ann. Mines*, 1859, [5], **15**, 221.
[3] Venable and Clarke, *J. Amer. Chem. Soc.*, 1896, **18**, 434.
[4] Ouvrard, *Compt. rend.*, 1891, **113**, 80.
[5] Moissan and Williams, *ibid.*, 1897, **125**, 629 ; Moissan, *Electric Furnace*, English translation (Williams & Norgate), 1908.
[6] Guertler, *Zeitsch. anorg. Chem.*, 1904, **40**, 337.
[7] See also Ditte, *Compt. rend.*, 1873, **77**, 783.
[8] See also Benedikt, *Ber.*, 1874, **7**, 703 ; Ditte, *loc. cit.*
[9] See also Ouvrard, *Compt. rend.*, 1901, **132**, 257.
[10] Rose, *Annalen*, 1852, **84**, 220 ; Laurent, *Jahresber.*, 1850, 257 ; Ditte, *Ann. Chim. Phys.*, 1883, [5], **30**, 248.
[11] Levi and Castellanni, *Atti R. Accad. Lincei*, 1908, [5], **17**, ıı, 613.

STRONTIUM AND ALUMINIUM.

Strontium Aluminates.—By the action of cold strontium hydroxide solution on metallic aluminium, or of excess of caustic potash on a hot solution of strontium chloride and potassium aluminate, a comparatively stable, crystalline tristrontium aluminate, $Sr_3(AlO_3)_2.6H_2O$, is obtained.[1] There is probably also a gelatinous compound of approximate composition, $Sr(AlO_2)_2.5H_2O$.[1]

STRONTIUM AND IRON.

Strontium Ferrate, $SrFeO_4$, mixed with ferric oxide, is obtained as a red powder by precipitation of strontium bromide with potassium ferrate. It is slightly soluble in water with decomposition, but insoluble in alcohol and ether.[2] It is decomposed by acids, with evolution of oxygen and formation of the corresponding ferric and strontium salts. The solid evolves oxygen when gently heated.

DETECTION AND ESTIMATION OF STRONTIUM.

Dry Tests.—Volatile strontium salts give to the non-luminous flame a carmine-red coloration. The most sensitive lines of the flame spectrum have the wave-lengths 6045 Å and 4608 Å.[3] According to de Gramont[4] the most sensitive rays photographically are: 4607·3, 4305·5, 4215·5, and 4077·8 Å.

When heated with sodium carbonate on charcoal, strontium salts give the white infusible oxide which is brightly luminescent whilst hot.

Wet Tests.— The spectroscopic method has been applied to solutions. An arc showing the following lines may be obtained between an iridium cathode and the surface of a strontium solution of concentration as low as 0·003 mgm. per c.c.: 4216 Å, and, more faintly, 5950, 4608, and 4078 Å.[5]

The conditions of precipitation of the alkaline earths as carbonates have already been discussed under calcium. From the acetic acid solution of the carbonates barium is removed as the chromate by the addition of potassium chromate or dichromate. Strontium may then be detected in the filtrate by various methods. The addition of ammonia[6] or alcohol,[7] or preferably both,[8] causes the precipitation of strontium chromate; or strontium sulphite may be precipitated by sodium sulphite in the presence of a little acetic acid[9] or alcohol;[10] or, finally, strontium sulphate may be precipitated in ammoniacal solution by ammonium sulphate, which dissolves calcium sulphate,[11] or by the addition of a

[1] Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 313.
[2] Eidmann and Moeser, *Ber.*, 1903, **36**, 2290.
[3] Riesenfeld and Wohlers, *ibid.*, 1906, **39**, 2628
[4] de Gramont, *Compt. rend.*, 1920, **171**, 1106.
[5] Riesenfeld and Pfützer, *Ber.*, 1913, **46**, 3140.
[6] Reichard, *Chem. Zeit.*, 1903, **27**, 877, 895, 913, 1035.
[7] Kolthoff, *Pharm. Weekblad*, 1920, **57**, 1080; van den Bos, *Chem. Weekblad*, 1913, **10**, 665.
[8] Caron and Raquet, *Bull. Soc. chim.*, 1906, [3], **35**, 1061.
[9] Hinds, *J. Amer. Chem. Soc.*, 1911, **33**, 510.
[10] Polonovski, *Bull. Soc. chim.*, 1922, [4], **31**, 806.
[11] Fresenius, *Zeitsch. anal. Chem.*, 1893, **32**, 194; Robin, *Compt. rend.*, 1903, **137**, 258; see also Paterson, *J. Amer. Chem. Soc.*, 1915, **37**, 2346.

saturated solution of calcium sulphate, which is more soluble than strontium sulphate.[1]

If the mixed carbonates be dissolved in nitric acid and the calcium nitrate removed by alcohol, or by alcohol and ether,[2] the remaining salts may be transformed into chlorides by heating with solid ammonium chloride,[3] and the strontium chloride, the presence of which will be indicated by the hygroscopicity of the residue, may then be dissolved out by alcohol and tested ; [4] or, alternatively, barium may be precipitated as chromate and strontium as sulphate.[5]

Strontium may be detected microchemically by a characteristic iodate or chromate precipitate,[6] or by the anhydrous chloride separated by absolute alcohol.[7]

A colour test may be used for the detection of strontium in presence of barium. If a little solid tannin and a few drops of an alkali hydroxide be added to the solution a bright green colour indicates strontium. It is a sufficiently delicate test to be obtained in a saturated solution of strontium sulphate.[8]

A detailed study of the different methods by which strontium may be obtained free from calcium and barium has been made by Sörensen.[9]

Quantitative Estimation of Strontium.—Strontium may be estimated quantitatively : as the sulphate, using a slight excess of dilute sulphuric acid or an alkali sulphate, and adding alcohol to diminish the solubility ; as the chromate, the solubility again being reduced by alcohol ; as the oxalate, when it may be weighed as the monohydrate, the anhydrous salt, or the oxide ; or, finally, as the carbonate, this method being more satisfactory than in the case of calcium, owing to the greater stability of strontium carbonate.[10]

When only small amounts of strontium are present, for example in silicate analysis, calcium and strontium are usually precipitated together as oxalates. When a considerable proportion of calcium is present the precipitation of strontium is practically perfect, irrespective of the amount of ammonium chloride present, so long as a sufficient excess of ammonium oxalate is employed. If barium be present, separation from it can be effected without much difficulty. The calcium and strontium may be afterwards transformed into nitrates, the calcium extracted by a mixture of alcohol and ether, as in the Fresenius method, and the strontium ultimately weighed as sulphate.[11]

In the presence of magnesium, calcium and strontium may be precipitated together as oxalates with the precautions already indicated under calcium.

Volumetric Methods may be used for the estimation of strontium.

[1] Gilmour, *Chem. News*, 1915, 111, 217 ; Raikow, *Zeitsch. anal. Chem.*, 1918, 57, 164.
[2] Fresenius, *Zeitsch. anal. Chem.*, 1893, 32, 189.
[3] Selvatici, *Chem. Zentr.*, 1910, i, 1109.
[4] Reichard, *Pharm. Zentr.*, 1915, 56, 329.
[5] Birnbräuer, *Chem. Zeit.*, 1911, 35, 755.
[6] Deniges, *Compt. rend.*, 1920, 170, 996 ; Bolland, *ibid.*, 1920, 171, 955 ; see also Schoorl, *Zeitsch. anal. Chem.*, 1909, 48, 401.
[7] Autenrieth, *Ber.*, 1904, 37, 3882.
[8] Schewket, *Biochem. Zeitsch.*, 1913, 54, 285.
[9] Sörensen, *Zeitsch. anorg. Chem.*, 1896, 11, 305 ; see also Richards and Yngve, *J. Amer. Chem. Soc.*, 1918, 40, 91.
[10] Winkler, *Zeitsch. angew. Chem.*, 1918, 31, i, 80, 83 ; van den Bos, *Chem. Weekblad*, 1911, 8, 5, see *J. Chem. Soc.*, 1911, 100, Abs ii, 228 ; Robin, *loc. cit.*
[11] Hillebrand, *J. Amer. Chem. Soc.*, 1894, 16, 83.

The oxalate may be precipitated in presence of alcohol or excess of ammonium oxalate, and titrated with permanganate, using sulphuric acid, or hydrochloric acid along with a manganese salt.[1] The strontium may also be precipitated as chromate by ammonium dichromate in ammoniacal solution in the presence of alcohol, and the excess of dichromate determined by titration, but the method is apparently only satisfactory when the strontium is free from barium and calcium.[2]

Titration by electrical conductivity measurements may be employed, the strontium being precipitated as chromate, sulphate, or oxalate.[3]

Electrolytic Methods have also been suggested.[4]

[1] Peters, *Amer J. Sci*, 1901, [4], **12**, 216 ; Averitt. *J Ind Eng. Chem*, 1917, **9**, 584 Averitt gives an indirect method for the estimation of a mixture of calcium and strontium by titration with permanganate

[2] Kolthoff, *Pharm Weekblad*, 1920, **57**, 972 , van den Bos, *loc. cit.*

[3] Dutoit and Mojoiu. *J. Chim. phys.*, 1910, **8**, 27.

[4] See Calcium.

CHAPTER IV.

BARIUM AND ITS COMPOUNDS.

BARIUM.

Symbol, Ba.   Atomic Weight, 137·37 (O=16).

Occurrence.—Barium forms 0·08 per cent. of the earth's crust,[1] and is therefore a less rare element than strontium.   Like the latter it is widely distributed in small quantities in both igneous[2] and sedimentary[3] rocks, and also in soils.[4]

The chief mineral is *barytes*, or *heavy spar*, $BaSO_4$, which occurs in veins often associated with lead.   The old lead mines of the north of England and of Shropshire are now reworked for barytes.   It is also found in some mineral waters.[5]

Next in importance is the carbonate, *witherite*, often found along with barytes.   There are also *barytocelestine*, the double sulphate of strontium and barium, *alstonite* and *barytocalcite*, both double carbonates of calcium and barium, and isomorphous with witherite, *psilomelane*, a barium manganite of composition approximately $(K_2,H_2,Mn,Ba)O.MnO_2$, and the silicates, *harmotome*, $H_2(K_2,Ba)Al_2Si_5O_{15}.4H_2O$, *brewsterite*, $H_4(Ba,Sr,Ca)Al_2Si_6O_{18}.3H_2O$, and *barytafelspar*, $K_2BaAl_4Si_{16}O_{48}$.[6]

Barium has been detected in various plants, for example tobacco,[7] and is present to some extent in the shells and skeletons of sea animals.   It is also present in the sun.[8]

History.—In 1602 a Bolognese shoemaker, Casciorolus, observed that heavy spar becomes phosphorescent when ignited with a combustible substance, and from that time Bolognian phosphorus became famous. Cronstedt called the mineral sulphate " marmor metallicum," and, in 1750, Marggraf found sulphuric acid in it but mistook the barium for calcium.   In 1774 Scheele,[9] whilst examining manganese ores containing barium, discovered the presence of an earth different from chalk, and described its chief properties.

[1] Clarke, *The Data of Geochemistry, Bull. U.S. Geol. Survey*, 1916, No. 616, p. 34.

[2] Dieulafait, *Ann. Chim. Phys*, 1878, [5], **15**, 540 ; Hillebrand, *J. Amer. Chem. Soc.*, 1894, **16**, 81.

[3] Collot, *Compt. rend.*, 1905, **141**, 832.

[4] Failyer, *U.S. Dept. Agric. Bur. Soils*, 1910, Bull. 72, see *J. Soc. Chem. Ind.*, 1910, **29**, 1218.

[5] Thorpe, *Phil. Mag.*, 1876, [5], **2**, 50 ; *Trans. Chem. Soc.*, 1881, **39**, 497 ; Richards, *Analyst*, 1901, **26**, 68 ; White, *ibid.*, 1899, **24**, 67.

[6] See Calcium and Strontium.

[7] Failyer, *loc. cit.* ; McHargue, *J. Amer. Chem. Soc.*, 1913, **35**, 826; Spallino, *Gazzetta*, 1913, **43**, ii, 475 ; Artis and Maxwell, *Chem. News*, 1916, **114**, 62.

[8] Rayet, *Ann. Chim. Phys.*, 1871, [4], **24**, 5 ; Lockyer, *Proc. Roy. Soc.*, 1869, **18**, 76.

[9] Scheele, *Chemical Essays*, Translation by Beddoes (Murray), 1786, Essay V, par. 32, p. 100.

In 1779 Guytan de Morveau proposed for the new earth the name " barote," on account of its great weight, and this was altered by Lavoisier to " baryta."

Withering, in 1782–1783, discovered the carbonate, afterwards named witherite after him, in the Leadhills in Scotland.

The metal, amalgamated with mercury, was first isolated by Davy in 1808,[1] and about the same time by Berzelius and Pontin.

Preparation of Barium.—As in the case of calcium and strontium, most of the earlier attempts to produce metallic barium only resulted in the formation of an amalgam with mercury, whether by electrolytic reduction of the oxide or chloride, using a mercury cathode,[2] or by reduction of the chloride by sodium amalgam,[3] or by reduction of the oxide with potassium, or of the chloride or iodide with sodium at red heat and subsequent extraction with mercury.[4] Attempts to isolate it by the reduction of a mixture of oxide and chloride,[5] or of the peroxide,[6] by aluminium, resulted only in the formation of alloys. The reduction of barium oxide by magnesium gave a product of doubtful composition.[7] Unsuccessful efforts have been made to separate barium directly by the electrolysis of fused barium chloride, with or without the addition of sodium chloride. Apparently only the subchloride is formed.[8]

Guntz made the first successful attempt to separate barium from mercury. By slow distillation at gradually increasing temperatures, he obtained a succession of amalgams richer and richer in barium. Finally, at a temperature of 950° C., a residue containing 98·3 per cent. of barium was left.[9] Later the method of separation of barium from mercury through the formation and subsequent decomposition of the hydride, as carried out in the case of strontium, was successfully applied.[10] Hydrogen was absorbed at 900° C., the mercury removed at 1200° C., just below the fusion point of the hydride, and; finally, the hydride decomposed *in vacuo* by further heating.

It was also found possible to apply the method, utilised later for strontium, of reduction of barium oxide at 1200° C., by aluminium powder.

A product of 98·8 per cent. purity was obtained. After redistillation *in vacuo* the metal was quite pure.[11]

Matignon obtained metallic barium by heating the oxide with silicon, or with ferrosilicon containing 95 per cent. of silicon, *in vacuo* at 1200° C.

$$3BaO + Si = BaSiO_3 + 2Ba - 37 \text{ Cal.}$$

[1] Davy, *Phil. Trans.*, 1808, 98, 343; *Alembic Club Reprints*, No. 6.

[2] Davy, *loc. cit.*; Hare, *J. prakt. Chem.*, 1840, [1], 19, 249; Bunsen, *Annalen*, 1854, 92, 251; Frey, *ibid.*, 1877, 183, 367; Maquenne, *Bull. Soc. chim.*, 1892, [3], 7, 367.

[3] Crookes, *Chem. News*, 1862, 6, 194; Donath, *Ber.*, 1879, 12, 745.

[4] Kern, *Chem. News*, 1875, 31, 244.

[5] Beketoff, *Annalen*, 1859, 110, 375.

[6] Stansfield, *Mem. Lit. Soc. Manchester*, 1902, 46, 1; *Ann. Chim. Phys.*, 1902, [7], 25, 284.

[7] Winkler, *Ber.*, 1890, 23, 126.

[8] Limb, *Compt. rend.*, 1891, 112, 1434; Lorenz and Clarke, *Zeitsch. Elektrochem.*, 1903, 9, 271.

[9] Guntz, *Compt. rend.*, 1901, 133, 872; *Bull. Soc. chim.*, 1903, [3], 29, 483.

[10] Guntz, *Compt. rend.*, 1905, 141, 1240; *Ann. Chim. Phys.*, 1905, [8], 4, 5.

[11] Guntz, *Compt. rend.*, 1906, 143, 339; *Ann. Chim. Phys.*, 1907, [8], 10, 437; see also Mallet, *Annalen*, 1877, 190, 62.

In spite of the large difference in the heats of formation of the oxides of barium and silicon, the barium, owing to its volatility, was separated, and a metal of 98·5 per cent. purity condensed.[1]

An attempt has also been made to separate metallic barium by electrolysing a pyridine solution of barium iodide, but the barium combined with pyridine, forming a reddish-brown spongy mass. By using a mercury cathode a 30 per cent. amalgam was obtained.[2]

Physical Properties.—Barium is a silver-white metal, not so soft as lead,[3] and of density 3·78.[4] It melts at about 850° C., is volatile at 950° C., and boils at 1150° C. *in vacuo.*[5] Its specific heat between −185° and +20° C. is 0·068.[6] The maximum photoelectric effect is produced in the red and orange part of the spectrum.[7] The ionic mobility of $\frac{1}{2}Ba^{\cdot}$ is 55.[8]

The following are the most intense lines in the spectrum measured in Ångström units [9] :—

Arc : Ultra-violet : 2304·3, 2335·4, 3071·7 ; Visible : 3891·9, 3910·0, 3935·9, 3993·6, 4130·8, 4283·3, 4350·6, 4402·8, 4554·2, 4579·8, 4726·6, 4900·1, 4934·2, 5424·8, 5519·4, 5535·7, 5777·9, 5800·3, 5826·5, 5853·9, 5971·9, 6019·7, 6063·3, 6111·0, 6141·9, 6497·1, 6595·6 ; Infra-red : 7060·2, 7229·2, 7280·6.

Spark : Ultra-violet : 2304·2, 2335·3, 2634·9, 2771·5, 3368·3, 3501·3 ; Visible : 3892·0, 3993·6, 4130·9, 4166·2, 4283·3, 4402·7, 4432·1, 4523·3, 4525·2, 4554·2, 4900·1, 4934·2, 5535·8, 5853·9, 6141·9, 6497·1, 6595·6, 6611·8.

Chemical Properties.—Barium may be kept unchanged in dry carbon dioxide, but readily tarnishes in the air owing to the formation of the oxide and nitride. If in the form of powder it may even take fire. It decomposes both water and alcohol, liberating hydrogen, but is unattacked by dry benzene, toluene, and petrol. It combines with ammonia and also with hydrogen. Its behaviour to most reagents is similar to that of calcium and strontium.[5]

The conditions have been studied under which barium, amalgamated with mercury, may be replaced by potassium or sodium from salt solutions in contact with it.[10]

Physiological Action.—Barium salts, especially the iodide and chlorate, are very toxic to both animals and plants.[11]

Atomic Weight.—*Approximate Atomic Weight.*—Early determinations gave to barium an equivalent of approximately 68·5, and its properties indicate a close connection with the divalent alkaline earth group, so that its atomic weight must be in the neighbourhood of 137.

[1] Matignon, *Compt. rend.*, 1913, 156, 1378.
[2] von Hevesy, *Zeitsch. Elektrochem.*, 1910, 16, 672.
[3] Guntz, *Compt. rend.*, 1901, 133, 872.
[4] Guntz, *ibid.*, 1905, 141, 1240.
[5] Guntz, *Bull. Soc. chim.*, 1903, [3], 29, 483 ; *Ann. Chim. Phys.*, 1905, [8], 4, 5.
[6] Nordmeyer and Bernouilli, *Ber.*, 1907, 5, 175.
[7] Case, *Phys. Review*, 1921, [2], 17, 398.
[8] Kohlrausch, *Zeitsch. Elektrochem.*, 1907, 13, 343 (footnote).
[9] Marshall Watts, *Index of Spectra* (Wesley & Son, London ; Abel Heywood & Son, Manchester), Appendices " U " (1911), " V " (1913), " W " (1914). See also *Tables Annuelles de constantes et de Données Numériques* (Gauthier-Villars et Cie), 1913–1916, vol. iv, pp. 384, 388, 389.
[10] Smith, *J. Physical Chem.*, 1905, 9, 13 ; but see Fernekes, *ibid.*, 1904, 8, 566.
[11] Coupin, *Compt. rend.*, 1900, 130, 791.

Exact Atomic Weight.[1]—The earliest determinations were made by Berzelius from the analysis of barium carbonate. He also found the ratio of barium chloride to silver chloride precipitated from it, and of barium chloride to barium sulphate, but his values varied through a wide range and have only a historical significance. The results of the earlier determinations are summarised in the following table :—

Year.	Investigator	Number of Experiments.	Ratio Measured		Atomic Weight.[1]
1826	Berzelius [2] .		$BaCl_2 . 2AgCl$	$=100 . 138\cdot07$	134 5
,,	,,	..	$BaCl_2 : BaSO_4$	$=100 : 112\cdot175$	134 8
1829	Turner [3]		$BaCl_2 : BaSO_4$	$=100 : 112\ 19$	134·6
,,	,,	..	$BaCl_2 : 2AgCl$	$=100 : 137\ 63$	137 4
1845	Pelouze [4]	3	$BaCl_2 : 2AgCl$	$=100 : 137\ 73$	137 2
1848	Marignac [5]	11	$BaCl_2 : 2Ag$	$=100 : 103\ 772$	137 0
1851	Struve [6]	..	$BaCl_2 : BaSO_4$	$=100 : 112\ 094$	137 1
1858	Marignac [7]	6	$BaCl_2.2H_2O : 2Ag$	$=100 : 88\ 406$	137 0
,,	,,	3	$BaCl_2 . 2Ag$	$=100 : 103\ 76$	137 0
,,	,,	3	$BaCl_2 . BaSO_4$	$=100 : 112\ 007$	138 5
1859	Dumas [8] .	16	$BaCl_2 . 2Ag$	$=100 : 103\ 84$	136·86

In 1893 Richards published an extensive series of carefully conducted determinations of the ratio of anhydrous barium bromide to the amount of silver required to precipitate the bromine in it, and of barium bromide to the amount of silver bromide precipitated by it.[9] The mean value of the former was found to be 137 747 : 100, and of the latter 137 749 : 174 080, giving atomic weights 137 38 and 137 37 respectively.[1]

Later he used barium chloride instead of the bromide, and obtained as the mean of ten determinations of the ratio $2AgCl : BaCl_2$, 100 : 72 654, and as the mean of fourteen determinations of the ratio $2Ag : BaCl_2$, 100 : 96 522.[10] The atomic weights calculated from these values are 137 36 and 137·34 respectively.

The International Commission on Atomic Weights for 1909 adopted the value

$$Ba=137\cdot37,\text{ which is still retained (1925).}$$

Uses.—No use has been found for the metal alone, but it is thought that it may prove of some value as a component of bearing

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[1] All atomic weights in this section have been recalculated from the experimental data given in the original memoirs, using the following atomic weight values :—

$$O= 16\cdot000$$
$$Cl= 35\cdot457$$
$$Br= 79\cdot916$$
$$Ag=107\cdot880$$
$$S= 32\cdot065$$

[2] Berzelius, *Pogg. Annalen*, 1826, 8, 189 ; see also Wollaston, *Phil. Trans.*, 1814, 104, 20.

[3] Turner, *Phil. Trans.*, 1829, 119, 296 ; 1833, 123, 537.

[4] Pelouze, *Compt. rend.*, 1845, 20, 1047.

[5] Marignac, *Annalen*, 1848, 68, 214.

[6] Struve, *ibid.* 1851, 80, 204.

[7] Marignac, *ibid.*, 1858, 106, 167.

[8] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 137.

[9] Richards, *Proc. Amer. Acad.*, 1893, 28, 1 ; 29, 55 ; *Zeitsch. anorg. Chem.*, 1893, 3, 441.

[10] Richards, *Zeitsch. anorg. Chem.*, 1894, 6, 89.

metals. Its use in the production of photoelectric cells has also been suggested.[1]

Alloys.—Some of the attempts to prepare metallic barium resulted in the formation of alloys of barium with zinc, tin, bismuth, aluminium, magnesium, nickel, and possibly iron, but these have not been studied.[2] A barium-cadmium alloy has also been prepared.[3] Amalgams of mercury and barium have been studied by Kerp and Böttger, who came to the conclusion that between 0° C. and 30° C. the stable solid phase is $BaHg_{13}$, and between 30° C. and 100° C., $BaHg_{12}$. It is possible that the compound $BaHg_{16}$ may exist below 0° C.[4]

Bearing metals consisting of lead mixed with a small percentage of alkaline earth metals have already been described under calcium alloys. Micrographic study of Frary metal, prepared by electrolysing a fused bath of barium and calcium chlorides with a molten lead cathode and graphite anode, shows the presence of crystals of the compounds Pb_3Ca and Pb_3Ba.[5] An alloy of lead and barium alone also contains Pb_3Ba and an eutectic mixture of this compound with pure lead, melting at 282° C., and containing 4 5 per cent. of barium.[6]

As in the case of calcium and strontium, some of the alloys, for example those with lead and tin, may prove useful in metallurgy as deoxidisers.[7]

COMPOUNDS OF BARIUM.

In common with the other alkaline earths, barium behaves generally as a divalent element. In its salts it forms a colourless divalent ion. Abel observed a catalytic effect produced by the barium ion in certain oxidation processes, such as the oxidation of sodium thiosulphate by hydrogen peroxide, and ascribed this to the formation of a quadrivalent barium ion. It seemed probable that calcium and strontium behave similarly.[8]

Certain acids are frequently prepared by treating the barium salts with sulphuric or phosphoric acid.

BARIUM AND HYDROGEN.

Barium Hydride, BaH_2, was first obtained by the action of magnesium on barium oxide at red heat in an atmosphere of hydrogen. An impure product, to which Winkler ascribed the formula BaH,[9] was formed, but Guntz showed that it was probably a mixture of equivalent quantities of the hydride BaH_2 and barium oxide.[10] It may be prepared

[1] Case, *Phys. Review*, 1921, [2], 17, 398.
[2] See Preparation; also Caron, *Compt. rend.*, 1859, 48, 440; Guntz, *ibid.*, 1903, 136, 749; *Ann. Chim. Phys.*, 1905, [8], 4, 5; 1907, [8], 10, 437.
[3] Gautier, *Compt. rend.*, 1902, 134, 1108.
[4] Kerp and Böttger, *Zeitsch. anorg. Chem.*, 1900, 25, 44; see also Kerp, *ibid.*, 1898, 17, 284; Fernekes, *J. Physical Chem*, 1904, 8, 566.
[5] Cowan, Simpkins, and Hiers, *Trans. Amer. Electrochem. Soc.*, 1921, 40, 27; see also Czochralski, *Zeitsch. Metallkunde*, 1920, 12, 371; *Chem. Abs.*, 1921, 15, 662.
[6] Czochralski and Rassow, *Zeitsch. Metallkunde*, 1920, 12, 337; *Chem. Abs.*, 1921, 15, 662.
[7] Vickers, *Metals and Their Alloys* (Crosby Lockwood & Son), 1923, p. 46.
[8] Abel, *Monatsh.*, 1913, 34, 171.
[9] Winkler, *Ber.*, 1891, 24, 1977.
[10] Guntz, *Compt. rend.*, 1906, 143, 339.

by the action of hydrogen on barium amalgam at a high temperature.[1] Hydrogen is absorbed by finely powdered barium even at 120° C., and at 170°–180° C. the reaction is vigorous.[2] Absorption by a cadmium-barium alloy begins at 350° C.[3]

The pure compound is crystalline, practically white, and of density 4 21. At 1400° C. it is slowly volatilised in a current of hydrogen. The heat of formation is 37 5 Cal. The temperature of fusion is in the neighbourhood of 1000° C. It is readily attacked by water and moist air, forming barium hydroxide, and by nitrogen above red heat. Molten barium hydride absorbs nitrogen.[4]

Barium hydride is the least stable of the three alkaline earth hydrides, and the difficulties encountered in studying the vapour pressures of calcium and strontium hydrides are increased in this case by the volatility of barium hydride.[5]

BARIUM AND THE HALOGENS.

Barium Subfluoride.—When metallic sodium is heated with barium fluoride at 800°–1000° C., a double compound of sodium fluoride and barium subfluoride, $NaF.BaF$, is obtained as a crystalline mass. It decomposes water, but only slowly, owing to the formation of insoluble barium fluoride.[6]

Barium Fluoride, BaF_2, may be obtained either by the action of a large excess of hydrofluoric acid on barium carbonate or oxide and calcination of the acid fluoride,[7] or by precipitation of a soluble barium salt with an alkali fluoride. If the latter method is employed in dilute boiling solution, a crystalline precipitate is formed.[8] Fine octahedral crystals may be obtained by fusing barium chloride with acid potassium fluoride, and washing with water.[9] Crystals may also be produced by heating the fluoride with dilute hydrochloric or nitric acid in a closed tube at 230°–240° C., or by slow evaporation of the aqueous solution.[10] Barium fluoride is also formed by the action of hydrofluoric acid gas on barium oxide or chloride.[9]

The heat of formation of barium fluoride is 226·68 Cal.[11] The density of the precipitated and calcined fluoride is 4·828.[12] The melting-point is 1289° C.[13]

Barium fluoride is not very soluble in water, although more so than the calcium salt. At 18° C. a saturated solution contains 18·3 milliequivalents per litre.[14] The heat of solution is −1·9 Cal.[11] It is some-

[1] Guntz, *Compt. rend.*, 1901, **132**, 963.

[2] Dafert and Miklauz, *Monatsh.*, 1913, **34**, 1685.

[3] Gautier, *Compt. rend.*, 1902, **134**, 1108.

[4] Guntz, *loc. cit.*; *ibid.*, 1903, **136**, 1071; *Ann. Chim. Phys.*, 1905, [8], **4**, 17; Gautier, *loc. cit.*

[5] Ephraim and Michel, *Helv. Chim. Acta*, 1921, **4**, 900.

[6] Guntz, *Compt. rend.*, 1903, **136**, 749; *Ann. Chim. Phys*, 1905, [8], **4**, 21.

[7] Berzelius, *Pogg. Annalen*, 1824, **1**, 18.

[8] Moissan, *Bull. Soc. chim.*, 1891, [3], **5**, 152.

[9] Poulenc, *Ann. Chim. Phys.*, 1894, [7], **2**, 27.

[10] Scheerer and Drechsel, *J. prakt. Chem.*, 1875, [2], **7**, 67.

[11] de Forcrand, *Compt. rend.*, 1911, **152**, 27.

[12] Schröder, *Jahresber.*, 1879, 31.

[13] Winter, *Dissertation*, Leipzig, 1913, 1; *J. Chem. Soc.*, 1914, **106**, Abs. ii, 126. Ruff and Plato found 1280° C. ±5°, *Ber.*, 1903, **36**, 2357.

[14] Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, **64**, 129.

what more soluble in acids and in a finely divided form is decomposed by hydrochloric and nitric acids under pressure at 230° C.

Acid Barium Fluoride is formed by the action of excess of hydrofluoric acid on the oxide or carbonate,[1] and on being calcined it gives the neutral fluoride. It is also formed by the action of hydrofluoric acid on barium fluoride.[1]

Barium Subchloride, BaCl, is obtained by heating together barium and barium chloride at 850° C. It forms brown microscopic crystals which decompose water with the evolution of hydrogen.[2] It is also formed in the electrolysis of barium chloride, using a carbon anode.[3]

By heating barium chloride with excess of sodium at 1000° C., a double salt, NaCl.BaCl, is formed. By shaking this with mercury, decomposition must take place because barium amalgam is obtained.[4] If the double salt be heated *in vacuo* at 700° C., sodium volatilises and barium chloride is left.[2] By heating the subchloride strongly, barium volatilises and the chloride remains.[2] By heating to redness in hydrogen or nitrogen, the hydride and nitride respectively are formed.[2]

Haber and Tolloczko represent the reactions between barium and chlorine by the following thermochemical equations[5] :—

$$Ba + Cl \quad = BaCl + 115 \cdot 8 \text{ Cal.}$$
$$BaCl + Cl \quad = BaCl_2 + 81 \cdot 2 \text{ Cal.}$$
$$Ba + BaCl_2 = 2BaCl + 34 \cdot 6 \text{ Cal.}$$
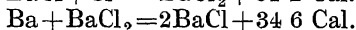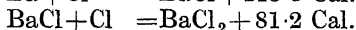
According to Marino,[6] the behaviour of these compounds may be explained by supposing them to be solid solutions of metallic barium or sodium, or suspensions of pulverised metal, in the ordinary barium chloride.

Barium Chloride, BaCl₂, was first described by Scheele. It may be formed from the metal by direct combination with chlorine ; from barium oxide by the action of chlorine[7] at red heat, or of hydrochloric acid ;[8] from barium sulphate by heating to redness in hydrochloric acid gas,[9] or by fusing with excess of ammonium chloride ;[10] and from barium hydroxide, carbonate, or sulphide by the action of aqueous hydrochloric acid, evaporation to dryness, and fusion in an atmosphere of hydrochloric acid gas to remove the last traces of moisture.[11]

On a commercial scale it may be prepared from the sulphate, barytes, by fusion with calcium chloride alone, or with carbon[12] or iron,[13] or a mixture of manganese chloride and carbon ;[14] by the action of hydrochloric acid on a mixture of barium sulphate and carbon at red heat ; or,

[1] Frémy, *Ann. Chim. Phys.*, 1856, [3], **47**, 12.

[2] Guntz, *Compt. rend.*, 1903, **136**, 749 ; *Ann. Chim. Phys.*, 1905, [8], **4**, 21.

[3] Limb, *Compt. rend.*, 1891, **112**, 1434 ; Haber and Tolloczko, *Zeitsch. anorg. Chem.*, 1904, **41**, 423 ; Haber, *Ann. Physik*, 1908, **26**, 927.

[4] Kern, *Chem. News*, 1875, **31**, 243.

[5] Haber and Tolloczko, *loc. cit.*

[6] Marino, *Atti R. Accad. Lincei*, 1915, [5], **24**, ii, 143.

[7] Weber, *Pogg. Annalen*, 1861, **112**, 619.

[8] Veley, *Ber.*, 1896, **29**, 580.

[9] Boussingault, *Compt. rend.*, 1874, **78**, 593.

[10] Rose, *Pogg. Annalen*, 1848, **74**, 564.

[11] Richards, *Zeitsch. anorg. Chem.*, 1894, **6**, 89.

[12] Godin, *Dingl. poly. J.*, 1864, **171**, 316 ; Mactear, *ibid.*, 1887, **262**, 288.

[13] d'Heureuse, *Pogg. Annalen*, 1848, **75**, 276.

[14] Kuhlmann, *Ann. Chim. Phys.*, 1858, [3], **54**, 386 ; *Compt. rend.*, 1858, **47**, 403, 464, 674.

finally, by reduction to sulphide and fusion with magnesium chloride under pressure.[1] If witherite form the starting-point, it may be fused with ammonium chloride or calcium chloride.

Barium chloride may be purified by repeated precipitation with alcohol.[2]

The heat of formation of barium chloride is 197·08 Cal.[3] The density of the salt dried at 220° C. is 3·856 at 24° C.[4] The melting-point is 958·9° C.,[5] and there is a transition point to another form at 924·5° C.[6] The specific heat is 0·0902.[7]

The specific electrical conductivity at the melting-point is 1·91 reciprocal ohms, and increases to 2·31 at 1100° C.[8]

The highest value found for the decomposition potential of barium chloride is 3·3 volts, but this is probably too low owing to the difficulty of avoiding polarisation.[9]   At 650° C. the value for barium chloride, mixed with lithium chloride to reduce the temperature of fusion, is 3·05 volts,[10] and at 750° C., 1·45 volts.

By heating with bromine at 200°–300° C., part of the chlorine is removed.[11] At the temperature of fusion it is partly decomposed by oxygen or by sulphur with loss of chlorine.[12] It is decomposed by water vapour with the formation of hydrochloric acid, but less readily than the other alkaline earth chlorides.[13]

Barium chloride is readily soluble in water, and the heat of solution is 1 92 Cal.[3] Its solubility has been studied by a number of investigators,[14] and the following values were given by Mulder[15]:—

Temperature, °C.	10	20	30	40	50	60	70	80	90	100
Grams BaCl₂ in 100 grams water.	33·3	35 7	38 2	40·8	43·6	46 4	49·4	52·4	55·6	58·8

Values for the solubility at higher temperatures were obtained by Etard.[16]

Temperature, °C.	100	130	144	160	180	215
Grams BaCl₂ in 100 grams solution	36·0	37·3	37·5	38 9	40·7	43·1

[1] Heinz, German Patent, 186738 (1907).

[2] Richards, Zeitsch. anorg. Chem., 1893, 3, 441.

[3] de Forcrand, Compt. rend., 1911, 152, 27.

[4] Richards, Zeitsch. anorg. Chem., 1894, 6, 89.

[5] Plato, Zeitsch. physikal. Chem., 1907, 58, 359 ; see also Winter, Dissertation, Leipzig, 1913, 1 ; J. Chem. Soc., 1914, 106, Abs. ii, 126 ; Gemsky, Jahrb. Min. Beilagebd., 1913, 36, 513 ; Arndt, Zeitsch. Elektrochem., 1906, 12, 337 ; Haber and Tolloczko, Zeitsch. anorg. Chem., 1904, 41, 412 ; Ruff and Plato, Ber., 1903, 36, 2357.

[6] Plato, loc. cit. ; Vortisch, Jahrb. Min. Beilagebd., 1914, 38, 185.

[7] Kopp, Annalen Suppl., 1864–5, 3, 293 ; see also Regnault, Ann. Chim. Phys., 1841, [3], 1, 129.

[8] Arndt, loc. cit.

[9] Arndt and Willner, Zeitsch. Elektrochem., 1908, 14, 216.

[10] Neumann and Bergve, ibid., 1915, 21, 152.

[11] Berthelot, Ann. Chim. Phys., 1883, [5], 29, 346 ; Potilitzin, J. Russ. Phys. Chem. Soc., 1882, 14, 82 ; Ber., 1882, 15, 918.

[12] Vogel, Schweigger's J., 1817, 21, 72.

[13] Kraus, Pogg. Annalen, 1838, 43, 138.

[14] Gay-Lussac, Ann. Chim. Phys., 1819, [2], 11, 309 ; Mulder, Jahresber., 1864, 92 ; Nordenskjöld, Pogg. Annalen, 1869, 136, 309 ; Gérardin, Ann. Chim. Phys., 1865, [4], 5, 142 ; Engel, ibid., 1888, [6], 13, 371 ; Kremers, Pogg. Annalen, 1856, 99, 444.

[15] Mulder, loc. cit.

[16] Etard, Ann. Chim. Phys., 1894, [7], 2, 535.

The solubility is considerably diminished in presence of hydrochloric acid,[1] sodium chloride,[2] or barium nitrate,[3] due to the action of a common ion. Engel found that, whereas 10 c.c. of pure water dissolve 28·9 milli-equivalents of barium chloride, 10 c.c. of hydrochloric acid solution, containing 50·5 milli-equivalents of acid, only dissolve 0·29 milli-equivalents of the salt.

Values for the solubility in different water-alcohol mixtures have also been determined,[4] but it is almost insoluble in absolute alcohol.[5] It is soluble in methyl alcohol to the extent of 2·18 parts in 100 parts of alcohol at 15·5° C.[6]

The aqueous solutions of barium chloride have been studied from the point of view of density,[7] specific heat,[8] refractivity,[9] vapour pressure,[10] boiling-points,[11] freezing-points.[12] viscosity,[13] compressibility,[14] and electrical conductivity.[15]

Determinations of the transport number of the barium ion in chloride solutions of different concentrations have been made,[16] and seem to indicate the presence of the complex ions $BaCl_3'$ and $BaCl_4''$.[17]

Powdered quartz absorbs barium chloride from its solutions.[18]

Hydrates of Barium Chloride.—Two hydrates of barium chloride, the mono- and the di-hydrate, have been isolated. On the ground of vapour pressure measurements, the existence of a hexahydrate, only stable in contact with the aqueous solution below about 10° C., has been suggested,[19] but the evidence scarcely seems sufficient to justify this supposition.

Barium Chloride Dihydrate, $BaCl_2.2H_2O$, separates from solution at ordinary temperatures in colourless monoclinic crystals [20] of density 3·097 at 24° C.[21] and specific heat 0·171.[22] The vapour pressure at 25° C. is

[1] Engel, *loc. cit.* ; Ditte, *Ann. Chim. Phys.*, 1881, [5], **22**, 564 ; see also Vitali, *Bull. Chim. Farm.*, 1907, **46**, 313.

[2] Precht and Wittjen, *Ber.*, 1881, **14**, 1667.

[3] Etard, *Ann. Chim. Phys.*, 1894, [7], **3**, 287.

[4] Schiff, *Annalen*, 1861, **118**, 365 ; Gérardin, *loc. cit.*

[5] Fresenius, *Annalen*, 1846, **59**, 127.

[6] Lobry de Bruyn, *Zeitsch. physikal. Chem.*, 1892, **10**, 783.

[7] Schiff, *Annalen*, 1859, **110**, 73 ; Bender, *Wied. Annalen*, 1887, **31**, 872 ; Kohlrausch, *ibid.*, 1879, **6**, 38 ; de Coppet, *Compt. rend.*, 1897, **125**, 533.

[8] Blümcke, *Wied. Annalen*, 1884, **23**, 161 ; Marignac, *Ann. Chim. Phys.*, 1876, [5], **8**, 410.

[9] Gladstone, *Trans. Chem. Soc.*, 1891, **59**, 589.

[10] Lescœur, *Compt. rend.*, 1887, **104**, 1511 ; Tammann, *Wied. Annalen*, 1885, **24**, 549 ; *Zeitsch. physikal. Chem.*, 1888, **2**, 42 ; Biltz, *ibid.*, 1902, **40**, 185.

[11] Gerlach, *Zeitsch. anal. Chem.*, 1887, **26**, 426 ; Kahlenberg, *J. Physical Chem.*, 1901, **5**, 339.

[12] Loomis, *Wied. Annalen*, 1896, **57**, 503 ; Jones and Chambers, *Amer. Chem. J.*, 1900, **23**, 89 ; Jones and Getman, *Zeitsch. physikal. Chem.*, 1903, **46**, 244 ; Rüdorff, *Pogg. Annalen*, 1872, **145**, 599 ; de Coppet, *Ann. Chim. Phys.*, 1872, [4], **25**, 524 ; **26**, 110.

[13] Arrhenius, *Zeitsch. physikal. Chem.*, 1887, **1**, 295 ; Wagner, *ibid.*, 1890, **5**, 31.

[14] Schumann, *Wied. Annalen*, 1887, **31**, 33.

[15] Kohlrausch and Grüneisen, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1215 ; Jones and Chambers, *loc. cit.* ; Jones and Getman, *Zeitsch. physikal. Chem.*, 1903, **46**, 267 ; Whetham, *Proc. Roy. Soc.*, 1903, **71**, 335 ; Kahlenberg, *loc. cit.*

[16] Bein, *Zeitsch. physikal. Chem.*, 1898, **27**, 1 ; Hopfgartner, *ibid.*, 1898, **25**, 115.

[17] Noyes, *ibid.*, 1901, **36**, 63.

[18] Thoulet, *Compt. rend.*, 1885, **100**, 1002.

[19] Lescœur, *loc. cit.*

[20] Kirschner, *Zeitsch. physikal. Chem.*, 1911, **76**, 177 (footnote).

[21] Richards, *Zeitsch. anorg. Chem.*, 1894, **6**, 89 ; see also Schiff, *Annalen*, 1859, **108**, 23.

[22] Kopp, *Annalen Suppl.*, 1864–5, **3**, 293.

5 8 mm.[1]   The heat of solution is -4.93 Cal.,[2] and the heat of hydration is 7 00 Cal.[2]   The dihydrate melts at $100°$ C., giving the anhydrous salt.

Barium Chloride Monohydrate, $BaCl_2.H_2O$.—The existence of this hydrate was first suspected by Thomsen,[4] because he found that the heat of reaction of anhydrous barium chloride with one grm.-mol. of water, 3 17 Cal., is less than half the heat of reaction with two grm.-mol.   Vapour pressure measurements also indicate its existence.[5]

It may be formed by heating the dihydrate at $60°$–$65°$ C.,[6] or by shaking the dihydrate with 99 per cent. of methyl alcohol, filtering at once through a Büchner funnel to remove undissolved salt, and leaving to crystallise.   After a few minutes the monohydrate separates from solution in colourless rhombic plates and can be dried over calcium chloride *in vacuo*.[7]   The vapour pressure of the monohydrate at $25°$ C. is 2·5 mm.[8]

Barium chloride may be used for softening boiler water, especially for removing permanent hardness.[9]

Addition Compounds.—Barium chloride absorbs ammonia under pressure, but gives it up again when exposed to the atmosphere.[10]   The compound, $BaCl_2.4NH_3$, is formed.   It has a dissociation pressure of 541 mm. of mercury at $0°$ C., and 1850 at $28·4°$ C.[11]   Ammonia also forms a compound with the double salt of mercury cyanide and barium chloride, $2Hg(CN)_2.BaCl_2.4NH_3$.[12]   Several addition compounds with ammonia derivatives have been isolated, with hydroxylamine, $BaCl_2.NH_2OH.2H_2O$[13] and $BaCl_2.NH_2OH$,[14] with glycine, $BaCl_2.2NH_2CH_2COOH$,[15] and with monobetaine, $BaCl_2.C_5H_{11}O_2N.4H_2O$.[16]

Double Salts.—The following double salts have been described (see next page).

Barium chloride forms mixed crystals in all proportions with lead chloride.[17]

Barium Bromide, $BaBr_2$, may be formed by the action of hydrobromic acid on barium carbonate,[18] by the precipitation of ferrous bromide with barium hydroxide or carbonate,[19] by the action of a solution of bromine on barium sulphide,[20] by the action of bromine on barium

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[1] Wilson, *J. Amer. Chem. Soc.*, 1921, **43**, 722 ; Partington, *Trans. Chem. Soc.*, 1911, **99**, 466 ; see also Foote and Scholes, *J. Amer. Chem. Soc.*, 1911, **33**, 1309 ; Frowein, *Zeitsch. physikal. Chem.*, 1887, **1**, 11 ; Lescœur, *Compt. rend.*, 1887, **104**, 1511 ; *Ann. Chim. Phys.*, 1889, [6], **16**, 378 , 1890, [6], **21**, 511 ; *Bull. Soc. chim.*, 1887, [2], **48**, 29. Schumb found 5·50 mm., *J. Amer. Chem. Soc.*, 1923, **45**, 342.

[2] Thomsen, *Thermochemistry*, English translation by Burke (Longmans, Green & Co.), 1908, p. 64 , Frowein, *loc. cit.*, found 3·815 Cal. per gram-molecule of water, or 7·63 for the total heat of hydration.

[3] Janecke, *Zeitsch. physikal. Chem.*, 1915, **90**, 267.

[4] Thomsen, *loc. cit.*

[5] Lescœur, *loc. cit.* ; Muller-Erzbach, *Ber.*, 1886, **19**, 127.

[6] Lescœur, *loc. cit.*

[7] Kirschner, *Zeitsch. physikal. Chem.*, 1911, **76**, 174.

[8] Foote and Scholes, *loc. cit.*

[9] Hundeshagen, *J. Soc. Chem. Ind.*, 1918, **37**, 670A.

[10] Weyl, *Pogg. Annalen*, 1864, **123**, 362.

[11] Joannis, *Compt. rend.*, 1891, **112**, 339.

[12] Varet, *Bull. Soc. chim.*, 1891, [3], **6**, 229 ; *Compt. rend.*, 1891, **112**, 1312.

[13] Antonow, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 476.

[14] Crismer, *Bull. Soc. chim.*, 1890, [3], **3**, 115.

[15] Pfeiffer and von Modelski, *Zeitsch. physiol. Chem.*, 1912, **81**, 329.

[16] Pfeiffer and von Modelski, *ibid.*, 1913, **85**, 1.

[17] Sandonnini, *Atti R. Accad. Lincei*, 1911, [5], **20**, ii, 646.

[18] Balard, *Ann. Chim. Phys.*, 1826, [2], **32**, 358

[19] Henry, *J. Pharm. Chim.*, 1829, [2], **15**, 52.

[20] Handl, *Sitzungsber. K. Akad. Wiss. Wien*, 1858, **32**, 244.

Salt	Remarks	Authority.
BaCl₂.2KCl.	M.-pt. 663° C	Gemsky, *Jahrb Min Beilagebd*, 1913, **36**, 513; Vortisch, *ibid*, 1914, **38**, 185
BaCl₂.ZnCl₂	.	Sandonnini, *Atti R Accad. Lincei*, 1912, [5], **21**, ii, 524.
BaCl₂ ZnCl₂.4H₂O	..	Ephraim and Model, *Zeitsch anorg. Chem.*, 1910, **67**, 379
BaCl₂.CuCl₂ ⎫ BaCl₂.2CuCl₂ ⎪ BaCl₂ CdCl₂ ⎬ BaCl₂ 2CdCl₂ ⎭	Obtained in a dissolved state only.	Varet, *Compt. rend*, 1896, **123**, 421
BaCl₂.2HgCl₂.2H₂O	.	Bonsdorff, *Pogg. Annalen*, 1829, **17**, 131, Varet, *loc cit.*; but see Foote and Bristol, *Amer Chem. J.*, 1904, **32**, 246.
BaCl₂.3HgCl₂ 6H₂O	Decomposes above 17·2° C.	Schreinemakers, *Chem. Week-blad*, 1910, **7**, 197; *J. Chem Soc*, 1910, **98**, Abs. ii, 488; Foote and Bristol, *loc. cit.*
BaCl₂.3HgCl₂.8H₂O	.	Swan, *Amer. Chem J*, 1898, **20**, 613.
BaCl₂ 2Hg(CN)₂ 5H₂O	..	Varet, *Compt. rend*, 1895, **121**, 348; *Ann Chim. Phys*, 1896, [7], **8**, 260.
BaCl₂.2Hg(CN)₂ 6H₂O	..	Dexter, *Amer. J. Sci*, 1862, [2], **33**, 121
BaCl₂.HgO.6H₂O.	Colourless needles. Loses nearly 5H₂O at 100° C., rest at 150° C	André, *Compt. rend.*, 1887, **104**, 431.
BaCl₂.MnCl₂	Probably only separated from fused mixture of two salts between 30 and 40 per cent. MnCl₂	Sandonnini, *Atti R. Accad. Lincei*, 1912, [5], **21**, i, 208.

hydroxide and extraction by alcohol of the bromide from admixture with bromate,[1] or, finally, by calcination of barium bromate.[2]   To obtain the anhydrous salt the solution formed by most of these methods is evaporated to dryness and heated to a little above 130° C.[3]   It is a white deliquescent substance of density 4·79 at 24° C.   It melts at 880° C.,[4] and sublimes at 820° C.[5]   The heat of formation is 179·82 Cal., and the heat of solution 4·98 Cal.[6]

The following values have been found for the solubility at different temperatures [7] :—

Temperature, °C.	−20	−9	+7	16	19	40	71	76	77	104	145	160	175
Grams BaBr₂ per 100 grams solution	45·7	46·5	48·5	48·8	49·3	50·9	55·1	55·5	55 6	56·6	60·5	59·4	60·3

[1] Henner and Hohenhauser, *Dingl. poly. J.*, 1864, **173**, 340.
[2] Richards, *Zeitsch. anorg. Chem.*, 1893, **3**, 441.
[3] Richards, *loc. cit.*; Kreider, *Amer. J Sci.*, 1905, [4], **20**, 97.
[4] Ruff and Plato, *Ber.*, 1903, **36**, 2357.   Kellner finds 847° C., *Zeitsch. anorg. Chem.*, 1917, **99**, 137.
[5] Stock and Heynemann, *Ber.*, 1909, **42**, 4088.
[6] de Forcrand, *Compt. rend.*, 1911, **152**, 27.
[7] Etard, *Ann. Chim. Phys.*, 1894, [7], **2**, 540; see also Kremers, *Jahresber.*, 1856, 274; *Pogg. Annalen*, 1856, **99**, 444; 1858, **103**, 57.

Milikan determined the concentration of solutions in contact with ice at different temperatures.

Temperature, °C.	−3 9	−14·1	−21·1
Grams $BaBr_2$ per 100 grams solution	17·8	38 2	44·6

The cryohydric temperature is −22·6° C., the concentration of the solution being 46·6 per cent. of barium bromide.[1]

The solubility is diminished by the presence of the barium or bromine ion. The effect of barium iodide has been studied by Etard.[2]

The properties of barium bromide solutions have been investigated from the point of view of density,[3] vapour pressure,[4] electrical conductivity,[5] freezing-point, and refractive index.[6]

An aqueous solution of barium bromide is decomposed by carbon dioxide with the formation of bromine and barium carbonate.

Barium bromide is soluble in both ethyl and methyl alcohol, but more so in the latter than the former.[7]

Hydrates of Barium Bromide.—From saturated solutions at ordinary temperatures the dihydrate separates out in rhombic[8] or monoclinic[9] crystals, which are rather hygroscopic, but do not liquefy under ordinary atmospheric conditions, and which have a density of 3 852 at 24° C.[10] At red heat the hydrated salt is slightly decomposed with loss of bromine.[11] It is isomorphous with barium chloride dihydrate. The solubility in methyl alcohol, which is considerable, decreases with the addition of water, reaching a minimum at about 50 per cent. of alcohol.[12]

The heat of solution of the dihydrate is −4 130 Cal.,[13] and, therefore, since the heat of solution of the anhydrous salt is 4·98 Cal., the heat of hydration is 9·11 Cal.

The dihydrate is in equilibrium with the monohydrate, $BaBr_2.H_2O$, at about 70° C.[10] In dry air the dihydrate may be reduced to the monohydrate at ordinary temperatures.[14] By heating to 100°–130° C. the anhydrous salt is obtained.[15]

Addition Compounds of Barium Bromide.—By the action of pure dry ammonia on dry barium bromide the compound $BaBr_2.8NH_3$ is formed. Its dissociation pressure is 760 mm. at 35·4° C.[16] An

[1] Milikan, *Zeitsch physikal. Chem.*, 1918, **92**, 78.

[2] Etard, *Ann. Chim. Phys.*, 1894, [7], **3**, 287.

[3] Gerlach, *Zeitsch. anal Chem.*, 1869, **8**, 285 ; Jones and Getman, *Zeitsch. physikal. Chem*, 1904, **49**, 407 ; de Coppet and Muller, *Compt. rend.*, 1902, **134**, 1208.

[4] Tammann, *Wied Annalen*, 1885, **24**, 552 ; *Zeitsch. physikal Chem.*, Ref., 1888, **2**, 45

[5] Jones and Getman, *loc. cit.* ; de Coppet and Muller, *loc. cit.*

[6] Jones and Chambers, *Amer. Chem. J.*, 1900, **23**, 89 ; Jones and Getman, *loc. cit.*

[7] Lobry de Bruyn, *Zeitsch. physikal. Chem.*, 1892, **10**, 783.

[8] Rammelsberg, *Pogg. Annalen*, 1864, **122**, 616 ; Handl, *Sitzungsber. K. Akad. Wiss Wien*, 1858, **32**, 244.

[9] Henner and Hohenhauser, *Jahresber.*, 1864, 148 ; Werther, *J. prakt. Chem.*, 1864, [1], **91**, 167, see *Jahresber.*, 1864, 189 ; Richards, *Zeitsch. anorg. Chem.*, 1893, **3**, 441.

[10] Richards, *loc. cit.*

[11] Schultze, *J. prakt. Chem.*, 1880, [2], **21**, 419.

[12] Lobry de Bruyn, *Zeitsch. physikal. Chem.*, 1892, **10**, 787.

[13] Thomsen, *Thermochemistry*, English translation by Burke (Longmans, Green & Co.), 1908, pp. 49, 58, 62.

[14] See also Guareschi, *Atti R. Accad. Sci. Torino*, 1913, **48**, 929.

[15] See also Beckmann, *J. prakt. Chem.*, 1883, [2], **27**, 152.

[16] Joannis, *Compt. rend.*, 1905, **140**, 1243 : but see Rammelsberg, *Pogg. Annalen*, 1842, **55**, 237.

addition compound with glycine is also formed, of composition $BaBr_2.2NH_2CH_2COOH.H_2O$.[1]

Double Salts.—The following double salts have been mentioned: $BaRhBr_5$,[2] $BaBr_2.HgBr_2$,[3] $BaBr_2.2Hg(CN)_2.6H_2O$ or $7H_2O$,[4] and $BaBr_2.2KBr$.[5]

Barium Perbromides.—The compound $BaBr_6$ is slowly formed when anhydrous bromine acts upon barium bromide.[6]

Solutions of barium bromide take up bromine, and experiments on the distribution of bromine between an aqueous barium bromide solution and a solvent immiscible with it, show that combination has taken place.[7] In solutions in which the barium bromide concentration was 0 09936 grm.-mol. per litre, the value of the dissociation constant for barium tetrabromide varied between 0·031 and 0·045 at 25° C.

If perbromides exist in the solid state they are very unstable.[8]

Barium Iodide, BaI_2, may be obtained by the neutralisation of hydriodic acid by barium carbonate, hydroxide, or sulphide. Instead of hydriodic acid, iodine and a reducing agent, for example iron[9] or barium sulphite, may advantageously be employed. By the action of iodine on barium hydroxide, barium iodide in solution and practically insoluble barium iodate are formed, and can be separated by filtration. Instead of removing barium iodate it may be reduced to barium iodide by sulphuretted hydrogen.[10] Barium iodide is also formed by the action of iodine on barium peroxide in the presence of water.[11] The anhydrous salt is obtained by evaporating to dryness and heating in a current of gaseous hydriodic acid.[12] It is a white, deliquescent compound of density 5·150 at 25° C.[13] and melting-point 740° C.[14] The heat of formation is 149·9 Cal.,[15] and the heat of solution 10 3 Cal.[16]

Barium iodide is very readily soluble in water, and the following values have been obtained[17] :—

Temperature, °C.	-22	-9	-5	15	32	40	67	87	96	113	140	165
Grams BaI_2 per 100 grams solution	58 5	60 0	60 9	66 0	68·3	69·8	71 9	72·1	72·7	73·6	73·7	74·1

The densities of solutions of different concentrations have been determined,[18] and also the electrical conductivities, refractive indices, and freezing-point lowerings.[19]

[1] Pfeiffer and von Modelski, *Zeitsch. physiol. Chem*, 1912, **81**, 329.
[2] Goloubkine, *Bull Soc. chim. Belg*, 1910, **24**, 388.
[3] Bonsdorff, *Pogg. Annalen*, 1830, **19**, 340.
[4] Varet, *Compt. rend.*, 1895, **19**, 398.
[5] Kellner, *Zeitsch. anorg. Chem.*, 1917, **99**, 137
[6] Berthelot, *Ann. Chim. Phys.*, 1883, [5], **29**, 348.
[7] Herz and Bulla, *Zeitsch. anorg. Chem.*, 1911, **71**, 254.
[8] Meyer, *ibid.*, 1902, **30**, 113.
[9] Compare Calcium Iodide.
[10] Kern, *Chem. News*, 1875, **31**, 244.
[11] Bodroux, *Compt. rend.*, 1906, **142**, 279.
[12] Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 113.
[13] Baxter and Brink, *J. Amer. Chem. Soc.*, 1908, **30**, 46
[14] Ruff and Plato, *Ber.*, 1903, **36**, 2357.
[15] de Forcrand, *Compt. rend.*, 1911, **152**, 27.
[16] de Forcrand, *loc. cit.* ; Tassilly, *loc. cit.*
[17] Etard, *Ann. Chim. Phys.*, 1894, [7], **2**, 544 ; see also Kremers, *Pogg. Annalen*, 1858, **103**, 57 ; **104**, 133.
[18] Kremers, *loc. cit.* ; Gerlach, *Zeitsch. anal. Chem.*, 1869, **8**, 285 ; Jones and Getman, *Zeitsch. physikal. Chem.*, 1904, **49**, 408 ; de Coppet and Muller, *Compt. rend.*, 1902, **134**, 1208.
[19] Jones and Getman, *loc. cit.*

The solubility is reduced by the presence of salts with a common ion.[1]   Barium iodide is readily soluble in alcohol.

A solution of pure barium iodide has a neutral reaction. When exposed to air and sunlight it soon becomes yellow and deposits barium carbonate.

Barium iodide is stable in dry air at ordinary temperatures, but when heated in air it ultimately gives up all its iodine and forms the oxide.[2]

It is sometimes used for therapeutic purposes.[3]

Hydrates of Barium Iodide.—There are apparently several hydrates, but they are difficult to identify on account of their deliquescent nature. The salt crystallising out at ordinary temperatures has been described as a heptahydrate, $BaI_2.7H_2O$,[4] but, according to Mügge,[5] commercial barium iodide, in large hexagonal prisms melting in the water of crystallisation at 25·7° C., is a hexahydrate, isomorphous with strontium chloride hexahydrate.   By evaporation of concentrated solutions Lescœur obtained a hexahydrate.[6]

There is also a very hygroscopic dihydrate which is rapidly coloured reddish brown in the air owing to the liberation of iodine.[7]   It is isomorphous with barium bromide dihydrate, and is apparently the stable form in contact with saturated solutions at 85° C.[8]   At 125° C. the higher hydrates are converted into the monohydrate, which begins to lose water and forms the anhydrous salt at 150° C.[9]

*   The heat of solution of the heptahydrate is -6.850 Cal.[10]

Addition Compounds.—Barium iodide forms addition compounds with ammonia containing 1, 2, 4, and 6 molecules of the latter respectively.   The compound, $BaI_2.6NH_3$, has a dissociation pressure of 50 mm. of mercury at 20° C., and the heat of formation from the iodide and ammonia is 10 80 Cal.[11]

Double Salts.—Barium iodide forms a number of double salts (see next page).

Barium Periodides.—By heating iodine with barium iodide, barium periodides similar to the calcium and strontium periodides can be obtained.[12]   Freezing-point determinations,[12] as well as distribution experiments,[13] indicate their presence in solution.   Herz and Bulla found that for a concentration of barium iodide of 0·1054 grm.-mol. per litre, and additional iodine 0 001683 to 0·01099 grm.-mol., the dissociation constant, assuming that only the tetra-iodide [14] is formed, is about 0·0007 at 25° C.[13]   Jakowkin considered that the compound

[1] See Barium Bromide.

[2] Schultze, *J. prakt Chem.*, 1880, [2], **21**, 419.

[3] Rothamel, *Annalen*, 1833, **5**, 353.

[4] Croft, *J. prakt. Chem.*, 1856, [1], 68, 402 ; Thomsen, *Ber.*, 1877, **10**, 1343 ; Beckmann, *J. prakt. Chem.*, 1883, [2], **27**, 144.

[5] Mügge, *Centr. Min.*, 1918, 105, see *J. Chem. Soc.*, 1918, **114**, Abs. ii, 313.

[6] Lescœur, *Ann. Chim. Phys.*, 1894, [7], **2**, 109 ; see also Milikan, *Zeitsch. physikal. Chem.*, 1918, **92**, 79.

[7] Werther, *J. prakt. Chem.*, 1864, [1], **91**, 331 ; see also Milikan, *loc. cit.*

[8] Etard, *loc. cit.*

[9] Beckmann, *loc. cit.*

[10] Thomsen, *Thermochemistry*, English translation by Burke (Longmans, Green & Co.), 1908, p. 49.

[11] Biltz, *Zeitsch. Elektrochem.*, 1920, **26**, 374.

[12] Meyer, *Zeitsch. anorg. Chem.*, 1902, **30**, 113.

[13] Herz and Bulla, *ibid.*, 1911, **71**, 254.

[14] See also Herz and Kurzer, *Zeitsch. Elektrochem.*, 1910, **16**, 869.

Salt.	Remarks	Authority.
$BaI_2 ZnI_2.4H_2O$.	.	Ephraim and Model, *Zeitsch.*
		anorg Chem , 1910, 67, 379.
$BaI_2.2ZnI_2$.	..	Rammelsberg, *Annalen*, 1838,
		28, 223
$BaI_2.HgI_2$	⎫	Boullay, *Ann Chim Phys* ,
$BaI_2.2HgI_2$ . . ⎬		1827, [2], 34, 352 , Berthemot.
$BaI_2.3HgI_2$ . . ⎭		*J. Pharm. Chim* . 1828, [2],
		14, 185.
$BaI_2 5HgI_2 8H_2O$	Density 4 63 at 0° C ⎫	
$2BaI_2.3HgI_2$.	.	Duboin, *Compt rend.*, 1906,
$2BaI_2.3HgI_2 16H_2O$	Large prisms, density ⎬	142, 887 See also Rohr-
	4 at 0° C⎸	bach, *Wied. Annalen*, 1883.
$3BaI_2 5HgI_2.21H_2O$	Very deliquescent pris- ⎰	20, 169
	matic crystals Den-	
	sity 4 06 at 0° C	
$BaI_2.HgI_2.5H_2O$.	Large flattened crystals,	Duboin, *Compt rend* , 1906,
	1–2 mm thick and	143, 313.
	2 cm long.	
$BaI_2.2Hg(CN)_2.4H_2O$.	.	Custer, *Arch Pharm* , 1848, [2],
		56, 1 ; but see Varet, *Compt.*
		rend., 1895, 121, 499
$BaI_2 2PbI_2.7H_2O$.	Yellowish-white crystals.	Mosnier, *Ann. Chim. Phys.*,
		1897, [7], 12, 396.
$2BaI_2.SbI_3.18H_2O$.	Transparent, deep	Schaefer, *Pogg. Annalen*, 1860.
	orange-red, rhombic	109, 611.
	prisms.	

BaI_6 is probably formed,[1] and in nitrobenzene solution indications of the existence of the compound BaI_{18} have been obtained.[2] According to recent investigations, each ion of the iodide is equally active in combining with molecules of iodine, hence in dilute solutions unsaturated with iodine, $Ba(I_3)_2$ appears to be the only polyiodide present. In more concentrated solutions the penta-iodide is also present.[3]

Mixed Halides of Barium.—By heating together manganese fluoride and barium chloride at 800°–1400° C., and purifying the product by repeated extraction with cold water, and finally, alcohol at 95° C., barium fluorochloride, $BaCl_2.BaF_2$, is obtained in colourless plates of density 4·51 at 18° C.[4] The melting-point is 1008° C.[5] It is unaffected by boiling alcohol, but decomposed into fluoride and chloride by water, especially if hot. It is soluble in concentrated hydrochloric and nitric acids, and decomposed by hot sulphuric acid. Barium fluorobromide, of density 4·96, and fluoro-iodide, of density 5 21, are similarly prepared.[4]

The fluorochloride may also be obtained by fusing the amorphous fluoride with alkali chlorides.[6]

A solution containing both barium chloride and bromide deposits mixed crystals of the composition $BaCl_xBr_y.2H_2O$,[7] but on fusing the

[1] Jakowkin, *Zeitsch. physikal. Chem.*, 1896, 20, 19.
[2] Dawson and Goodson, *Trans. Chem. Soc.*, 1904, 85, 796.
[3] Pearce and Eversole, *J. Physical Chem.*, 1924, 28, 245.
[4] Defacqz, *Compt. rend.*, 1904, 138, 197 ; Winter obtained a much higher value, 5·931, *Dissertation*, Leipzig, 1913, 1, see *J. Chem. Soc.*, 1914, 106, Abs. ii, 126.
[5] Winter, *loc. cit.* ; Plato, *Zeitsch. physikal. Chem.*, 1907, 58, 359.
[6] Poulenc, *Ann. Chim. Phys.*, 1894, [7], 2, 28.
[7] Herbette, *Compt. rend.*, 1906, 143, 243.

two salts together a molecular compound is formed with the evolution of heat.[1]

Mixed Perhalides of Barium.—The behaviour of iodine towards solutions of barium chloride, bromide, and iodide is similar to that of the corresponding calcium and strontium compounds. The following solubility data have been obtained [2] :—

| Solvent. | Water. | 10 per cent. solutions of | | |
		$BaCl_2$	$BaBr_2$	BaI_2
Grams iodine per 100 grams solvent.	0 0142	0·067	0 231	6·541
Temperature, °C. .	Ordinary temp.	18 5	13 5	13 5

OXYHALOGEN DERIVATIVES OF BARIUM.

Barium Oxychloride.—By the action of barium hydroxide on barium chloride in boiling aqueous solution, the compound $BaCl_2.BaO.5H_2O$, or mixed crystals of barium chloride and barium hydroxide, may separate, according to the proportions employed. The oxychloride crystallises in small pearly plates, which are attacked by water, alcohol, or carbon dioxide. *In vacuo* part of the water of crystallisation is lost. André at first gave the formula as $BaCl_2.BaO.8H_2O$, but later fixed the number of molecules of water as five.[3]

Barium Hypochlorite is not known in the pure state, but, when chlorine is allowed to react with crystallised barium hydroxide, an unstable compound similar to bleaching powder is obtained. It contains some hypochlorite, and is gradually transformed, on keeping, into a mixture of chloride and chlorate.[4]

Barium Chlorite, $Ba(ClO_2)_2$, is formed by the action of chloric acid on barium hydroxide in solution. It is an unstable salt, but it can be obtained in a fairly pure condition by rapid evaporation over a flame until a skin is formed, and then further concentration *in vacuo*. Slow evaporation results in the formation of the chlorate. Barium chlorite is very soluble in water, and is decomposed into chlorate and chloride at 235° C.[5]

Barium Chlorate, $Ba(ClO_3)_2$, is formed by the neutralisation of barium hydroxide or carbonate with chloric acid.[6] It may also be precipitated by the action of ammonium chlorate,[7] or aluminium

[1] Berthelot, *Ann. Chim. Phys.*, 1883, [5], **29**, 349.
[2] Meyer, *Zeitsch. anorg. Chem.*, 1902, **30**, 113.
[3] André, *Compt. rend.*, 1881. **93**, 58 ; *Ann. Chim. Phys.*, 1884, [6], **3**, 71 ; see also Beckmann, *Ber.*, 1881, **14**, 2156 ; *J. prakt. Chem.*, 1883, [2], **27**, 127 ; Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 53 ; Schreinemakers, *Zeitsch. physikal. Chem.*, 1909, 68, 88 ; Schreinemakers and Milikan, *J. Chem. Soc.*, 1912, **102**, Abs. ii. 760.
[4] Grouville, *Ann. Chim. Phys.*, 1821, [2], **17**, 39 : Könjgel-Weisberg, *Ber.*, 1879, **12**, 346.
[5] Millon, *Ann. Chim. Phys.*, 1843, [3], **7**, 327.
[6] Vauquelin, *Ann. Chim.*, 1815, [1], **95**, 100.
[7] Thompson, *Phil. Mag.*, 1847, [3], **31**, 510.

chlorate,[1] on barium carbonate, preferably in boiling alcohol. By the action of chlorine at 80° C. on barium hydroxide solution, or on barium carbonate suspended in water,[2] chlorate mixed with chloride is obtained. The latter can, for the most part, be removed by recrystallisation.

From solution the monohydrate separates out in colourless, monoclinic crystals.[3] The chlorates of the alkaline earths exhibit crystalloluminescence on crystallising out.[4] The density is 3·179,[5] and the specific heat 0·157.[6] The salt loses its water of crystallisation at 180° C.,[7] and slowly decomposes at 300°–310° C., with the formation of perchlorate and chloride and the loss of oxygen.[8] The rate of decomposition increases with rise of temperature, and the reaction continues until about 10 per cent. of oxygen has been lost.

When mixed with a reducing agent, barium chlorate readily explodes. It reacts with iodine, forming iodic and chloric acids and barium iodide.[9] With sulphurous acid at 60° C. barium sulphate and chlorine monoxide are obtained. Sulphuric acid decomposes it with the production of light. The heat of solution of the anhydrous salt is −6·7 Cal.[10] The heat of solution of the monohydrate is −11 24 Cal.,[11] and, therefore, the heat of hydration is 4 54 Cal.

The following values have been found for the solubility [12] :—

Temperature, °C.	−2 749±0 004 cryohydric point	0°	10°	20°	30°	40°	50°
Grams anhydrous salt per 100 grams solution.	15·28		16·9	21 23	25 26	29·43	33 16	36·69

	60°	70°	80°	90°	99·1°	105° boiling-point.
	40 05	43·04	45·90	48 47	51·17	52·67

The vapour pressures [13] and refractive indices [14] of barium chlorate solutions have been determined.

The salt is only slightly soluble in alcohol.

Barium chlorate is used in pyrotechnics for the production of green fire.

Barium Perchlorate, $Ba(ClO_4)_2$, may be obtained by the action of perchloric acid on barium hydroxide or carbonate,[15] or by the interaction of zinc perchlorate with barium hydroxide.[16] It is also formed by heating the chlorate (see Chlorate).

It forms hexagonal prisms containing 3 molecules of water.[17] It is not hygroscopic if free from perchloric acid, and is soluble in water and, alcohol.[18] It loses 2 molecules of water over concentrated sulphuric acid

[1] Brandau, *Ann. Pharm.*, 1869, **151**, 361.
[2] Grace-Calvert, *J. Chem. Soc.*, 1851, **3**, 106.
[3] Rammelsberg, *Pogg. Annalen*, 1853, **90**, 16 ; Souchay, *Annalen*, 1857, **102**, 381.
[4] Trautz and Anschütz, *Zeitsch physikal. Chem.*, 1906, **56**, 236.
[5] Schroeder, *Dichtigkeitsmessungen*, Heidelberg, 1873.
[6] Kopp, *Annalen Suppl.*, 1864–5, **3**, 298.
[7] Millon, *Ann. Chim. Phys.*, 1843, [3], **7**, 327.
[8] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1887, **19**, 339, see *Ber.*, 1887, **20**, Ref., 769.
[9] Potilitzin, *Ber.*, 1887, **20**, Ref., 772.
[10] Berthelot, *Ann. Chim. Phys.*, 1875, [5], **4**, 103.
[11] Berthelot, *loc. cit.* ; Thomsen, *Thermochemistry*, English translation by Burke (Longmans, Green & Co.), 1908, p. 50.
[12] Trautz and Auschutz, *loc. cit.* ; see also Kremers, *Jahresber.*, 1856, 274 ; Etard, *Ann. Chim. Phys.*, 1894, [7], **2**, 529.
[13] Tammann, *Zeitsch. physikal Chem.*, 1888, **2**, Ref., 45.
[14] Gladstone, *Trans. Chem. Soc.*, 1891, **59**, 595.
[15] Groth, *Pogg. Annalen*, 1868, **133**, 226.
[16] Henry, *Annalen*, 1839, **31**, 345.
[17] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1887, **19**, 339, see *Ber.*, 1887, **20**, Ref., 770.
[18] Sérullas, *Ann. Chim. Phys*, 1831, [2], **46**, 303.

at room temperature, becomes anhydrous at $100°$ C., and at $400°$–$460°$ C. it decomposes.[1]   The heat of solution of the anhydrous salt is $-1\ 8$ Cal., and of the trihydrate $-9\ 4$ Cal.[2]   Therefore the heat of hydration is $7\ 6$ Cal.   A dihydrate and a monohydrate have also been mentioned.[3]

The anhydrous salt is said to exist in two forms, the transition point being $284°$ C.[4]

Barium Oxybromide.—By the interaction of barium bromide and hydroxide in solution a crystallised oxybromide of composition $BaBr_2$. $BaO.5H_2O$,[5] or $7H_2O$,[6] is obtained.   On heating to $120°$ C. in dry air, 2 molecules[7] or 3 molecules[6] of water remain.   The compound is dissociated by water or alcohol, and decomposed by carbon dioxide.

Barium Hypobromite is probably formed in solution by the action of bromine on barium hydroxide.   The solution has oxidising properties, and has been employed to estimate ammonia by the liberation of nitrogen.[8]   Carbon dioxide causes the evolution of bromine and the precipitation of barium carbonate.   By distilling a dilute solution under reduced pressure, whilst at the same time carbon dioxide is passed through it, a distillate containing bromine and hypobromous acid is obtained.[9]   Bromine behaves in much the same way towards barium hydroxide as towards solid calcium hydroxide.[9]

Barium Bromate, $Ba(BrO_3)_2$, may be prepared by precipitation from boiling solutions of potassium bromate and barium chloride, or, preferably, acetate.[10]   It is also formed by the action of barium hydroxide on bromine chloride,[11] and by the action of bromine on a boiling solution of barium hydroxide.   It forms monoclinic prisms, of density 3.82, isomorphous with the chlorate[12] and containing 1 molecule of water of crystallisation, which is not removed until a temperature of $170°$ C. is reached.   At about $260°$ C. the salt begins to decompose.[13]   The decomposition apparently takes place in two stages, because there is an intermediate slowing down.   Potilitzin attributes this to the formation of two isomeric bromates, $BaO_2.Br_2O_4$ and $Ba(BrO_3)_2$, bromine being pentavalent in the first and heptavalent in the second.

The following values have been obtained for the solubility at different temperatures[14] :—

Temperature, °C.	-0.034 ± 0.002, cryohydric point	$0°$	$10°$	$20°$	$30°$	$40°$	$50°$	$60°$
Grams $Ba(BrO_3)_2$ per 100 grams solution	0.280	0.286	0.430	0.652	0.95	1.31	1.72	2.271

	$70°$	$80°$	$90°$	$98.7°$	$100.39°$ boiling-point	
	2.922	3.521	4.260	5.256	5.39	

[1] Potilitzin, *J. Russ. Phys. Chem. Soc*, 1887, **19**, 339, see *Ber.*, 1887, **20**, Ref., 770.
[2] Berthelot, *Ann. Chim. Phys*, 1875, [5], 5, 103
[3] Willard and Smith, *J. Amer. Chem. Soc*, 1923, **45**, 286.
[4] Vorlander and Kaascht, *Ber.*, 1923, **56**, [B], 1157.
[5] Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 55 ; *Compt. rend.*, 1895, **120**, 1338 ; Schreinemakers and Milikan, *J. Chem. Soc.*, 1912, **102**, Abs. ii, 760.
[6] Beckmann, *J. prakt. Chem.*, 1883, [2], **27**, 132.
[7] Tassilly, *loc. cit.*
[8] Knop, *Ber.*, 1870, **3**, 91.
[9] Dancer, *J. Chem. Soc.*, 1862, **15**, 477.
[10] Rammelsberg, *Pogg. Annalen*, 1841, **52**, 81.
[11] Balard, *Ann. Chim. Phys.*, 1826, [2], **32**, 367.
[12] Rammelsberg, *loc. cit* ; *Pogg. Annalen*, 1853, **90**, 17.
[13] Potilitzin, *loc. cit.*
[14] Trautz and Anschütz, *Zeitsch. physikal. Chem.*, 1906, **56**, 236 ; see also Harkins and Winninghoff, *J. Amer. Chem. Soc.*, 1911, **33**, 1827 ; Harkins, *ibid.*, 1836.

The solubility is increased by potassium nitrate and diminished by barium nitrate and potassium bromate.

Barium Perbromate, $Ba(BrO_4)_2$, is obtained as a white granular precipitate by the action of perbromic acid on barium chloride solution,[1] or in a crystalline form by mixing solutions of potassium perbromate and barium chloride and adding alcohol.[2] It is not formed by the decomposition of barium bromate by heat.

Barium Oxyiodide is formed similarly to the other oxyhalides.[3] It has the composition $BaI_2.BaO.9H_2O$. By heating to 120° C. it forms the pentahydrate,[4] and over sulphuric acid *in vacuo* the dihydrate.[5] It is decomposed by water, alcohol, and carbon dioxide.

Barium Iodate, $Ba(IO_3)_2$, is obtained by precipitating a soluble barium salt with sodium iodate in dilute boiling solutions,[6] by treating barium hydroxide with excess of iodic acid,[7] or by the action of iodine on powdered barium hydroxide.[8] The precipitate is composed of small opaque monoclinic prisms containing 1 molecule of water of crystallisation, but it may be obtained in clear crystals by recrystallisation from nitric acid. It is isomorphous with the bromate and chlorate,[9] loses its water at 180° C., and is decomposed by heat, giving off oxygen and iodine.[10] The decomposition takes place explosively in contact with carbon.[8] Sulphuric acid liberates iodine from barium iodate.[11]

The solubility, even in hot water, is only small.[12] In 100 grm. of the solution at 20° C. there is 0 022 grm. of the anhydrous salt.

Barium Periodate, $Ba(IO_4)_2$, has not been isolated in the solid state,[13] but several basic salts are known. The compound formed by precipitation of a barium salt by an alkali periodate in acid solution is $BaO.Ba(IO_4)_2.7H_2O$.[14] If the solution is strongly acid a pentahydrate[13] or, in presence of nitric acid, a trihydrate may be formed.[15] The heptahydrate loses 4 molecules of water at 200° C., and is completely dehydrated at 300° C.[13]

Ihre obtained also the compound $2BaO.Ba(IO_4)_2.6H_2O$.[14]

By calcination of the dibarium salt,[15] or by heating barium oxide, peroxide, or carbonate with iodine in the presence of air,[16] a pentabarium compound, $4BaO.Ba(IO_4)_2$, is obtained. It is also formed by heating barium iodate to a high temperature[16] when iodine and oxygen are evolved, or by heating barium iodide in dry air. Similar reactions take place with calcium and strontium compounds, but the products are less

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[1] Kämmerer, *J. prakt. Chem.*, 1863, [1], **90**, 190.

[2] Muir, *J. Chem. Soc.*, 1874, **27**, 324.

[3] Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 59 ; Beckmann, *J. prakt. Chem.*, 1883, [2], **27**, 134.

[4] Beckmann, *loc. cit.*

[5] Tassilly, *loc. cit.*

[6] Rammelsberg, *Pogg. Annalen*, 1838, **44**, 576 ; Ditte, *Ann. Chim. Phys.*, 1890, [6], **21**, 149.

[7] Millon, *Ann. Chim. Phys.*, 1843, [3], **9**, 416.

[8] Gay-Lussac, *Ann. Chim.*, 1814, [1], **91**, 60.

[9] Marignac, *Jahresber.*, 1856, 300.

[10] See Sugiura and Cross, *Trans. Chem. Soc.*, 1879, **35**, 118.

[11] Rammelsberg, *Pogg. Annalen*, 1839, **46**, 159 ; 1841, **52**, 411.

[12] Trautz and Anschutz, *loc. cit.* ; Harkins and Winninghoff, *loc. cit.* ; Harkins, *loc. cit.*

[13] Rammelsberg, *Jahresber.*, 1867, 168.

[14] Ihre, *Ber.*, 1870, **3**, 316.

[15] Langlois, *Ann. Chim. Phys.*, 1852, [3], **34**, 265.

[16] Rammelsberg, *Ber.*, 1869, **2**, 147 ; Cross and Sugiura, *loc. cit.* ; *Trans. Chem. Soc.*, 1878, **33**, 409.

stable. Rammelsberg obtained several other salts of doubtful composition,[1] and Langlois isolated the compound $3BaO.2Ba(IO_4)_2.5H_2O$.[2]

BARIUM AND MANGANESE.

Barium Manganites.—It is probable that many natural double oxides are really manganites very rich in manganese, for example *psilomelane*, and *varvacite*, $Mn_9O_{18}Ba.3H_2O$.[3] Several manganites have been prepared artificially. The compound $BaO.MnO_2$ is stable above 1100° C. or below 1000° C., and the compound $BaO.2MnO_2$ between these two temperatures. The latter is also formed along with manganese dioxide by heating barium permanganate at 320° C., and if the heating be prolonged, a manganite still richer in manganese, $BaO.7MnO_2$, is obtained.[4] The compounds, $BaO.5MnO_2$[5] and $BaO.MnO_2.H_2O$,[6] have also been obtained.

Barium Manganate is used as a colouring matter under the name of Cassels' green, manganese green, or Rosensthiel's green. The composition depends on the method of preparation. Insoluble hexagonal plates of $3BaO.2MnO_3$ are formed by heating a mixture of barium oxide and nitrate with manganese oxide,[7] or barium peroxide with manganese dioxide, or carbonate,[8] or by the action of hydrogen peroxide on the permanganate.[9]

An impure manganate of formula $BaMnO_4$, containing no water of crystallisation, is obtained by precipitating barium chloride with potassium manganate.[6] It is also formed by heating pure manganese dioxide with potassium chlorate and barium hydroxide,[10] or by heating the manganite above 1500° C.[11]

By heating a mixture of permanganate and barium hydroxide the compound, $Ba_3Mn_2O_8.H_2O$, which does not lose its water at red heat, is formed.[12]

Barium Permanganate, $Ba(MnO_4)_2$, is obtained in fine orthorhombic octahedra, which are deliquescent and almost black with violet reflections,[13] by saturating a solution of potassium permanganate with hydrofluosilicic acid, treating with a suspension of barium hydroxide, and crystallising.[14] It may also be prepared by the action of barium nitrate and barium hydroxide on potassium permanganate and subsequent treatment with carbon dioxide.[15] Other methods are unsatisfactory.[16]

[1] Rammelsberg, *Jahresber*, 1867, 168.
[2] Langlois, *Ann. Chim. Phys*, 1852, [3], **34**, 265.
[3] Walker, *Amer. Chem. J.*, 1888, **10**, 41
[4] Rousseau and Sagher, *Compt. rend.*, 1884, **99**, 139; Rousseau, *ibid.*, 1886, **102**, 425, 615; 1887, **104**, 786, 1796.
[5] Risler, *Bull. Soc. chim.*, 1878, [2], **30**, 110; Rousseau, *Compt. rend.*, 1885, **101**, 167; Dufau, *Ann. Chim. Phys.*, 1897, [7], **12**, 257.
[6] Kassner and Keller, *Arch. Pharm.*, 1901, **239**, 473.
[7] Rosensthiel, *J. Pharm Chim.*, 1864, [3], **46**, 344.
[8] Donath, *Dingl. poly. J.*, 1887, **263**, 246
[9] Gorgeu, *Compt. rend.*, 1890, **110**, 958.
[10] Schafarik, *J. prakt. Chem.*, 1863, [1], **90**, 16.
[11] Rousseau, *Compt. rend.*, 1886, **102**, 616.
[12] Auger and Billy, *ibid.*, 1904, **138**, 500.
[13] Mitscherlich, *Pogg. Annalen*, 1832, **25**, 287; Chevillot and Edwards, *Ann. Chim. Phys.*, 1817, [2], **4**, 287; 1818, [2], **8**, 337.
[14] Rousseau and Bruneau, *Compt. rend.*, 1884, **98**, 229.
[15] Muthmann, *Ber.*, 1893, **26**, 1016.
[16] Böttger, *J. prakt. Chem.*, 1863, [1], **90**, 156; Fromherz, *Pogg. Annalen*, 1834, **31**, 677.

The electrical conductivities of different barium permanganate solutions have been determined.[1]

BARIUM AND OXYGEN.

Barium Suboxide, Ba_2O.—By heating barium oxide with metallic magnesium to 900°–1100° C., a blackish sintered residue, which reacts with water, producing hydrogen equivalent to half the barium employed, is obtained. A similar product is formed by heating together metallic barium and barium oxide. Guntz regarded it as the suboxide, Ba_2O.[2] It absorbs nitrogen and hydrogen at red heat. With hydrogen the reaction is

$$Ba_2O + H_2 = BaH_2 + BaO.$$
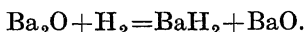
The mixture of barium hydride and oxide behaves as if it were the compound BaH.[3]

Barium suboxide dissociates into barium and barium oxide when strongly heated. If a volatile metal be used for the reduction, the dissociated barium volatilises with the excess of the reducing metal, forming an alloy. The temperature must be higher than that necessary to volatilise barium, in order to dissociate the suboxide. If a non-volatile metal, such as aluminium, be used, the suboxide is still the first product, but this splits up into barium oxide and barium, the latter distils off alone, and the remaining oxide is again reduced to the suboxide.[4]

Barium Oxide, BaO, may be formed by the direct combination of its elements. It is obtained by calcination of the hydroxide or nitrate. A high temperature is required to prevent contamination with the peroxide. Barium carbonate cannot be decomposed under the conditions prevailing in the limekiln. For production from witherite on the commercial scale it is necessary to heat with carbon, when the following reaction takes place[5] :—

$$BaCO_3 + C = BaO + 2CO.$$
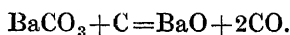
According to a patent of Frank's,[6] barium oxide may be obtained by heating together barium carbonate and carbide.

$$3BaCO_3 + BaC_2 = 4BaO + 5CO.$$
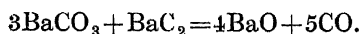
Barytes may be used instead of witherite, and is generally a purer mineral. By heating with coal or coke[7] in the reverberatory furnace, or preferably by using a gaseous reducing agent at 600°–650° C.,[8] barytes may be reduced to the sulphide, which can be readily converted into the hydroxide and thence into the oxide.

The United Barium Company at Niagara Falls patented a process for preparing barium oxide directly from barium sulphate. The sulphate is mixed with sufficient carbon to reduce a quarter of the sulphate to

[1] Franke, *Zeitsch. physikal. Chem.*, 1895, **16**, 463.
[2] Guntz, *Compt. rend.*, 1906, **143**, 339 ; *Ann. Chim. Phys.*, 1907, [8], **10**, 437.
[3] Winkler, *Ber.*, 1891, **24**, 1977; see Barium Hydride.
[4] See Preparation of Barium.
[5] Lunge, *Dingl. poly. J.*, 1871, **202**, 76 ; Rivière, *Bull. Soc Mulh.*, 1866, **36**, 438 ; Scheurer-Kestner, *ibid.*, 448.
[6] See Terres and Brückner, *Zeitsch. Elektrochem.*, 1920, **26**, 2.
[7] See also Mactear, *Dingl. poly. J.*, 1886, **262**, 287.
[8] Marino, *Gazzetta*, 1913, **43**, i, 416 ; Marino and Danesi, *ibid.*, 425, 434.

sulphide, and the whole is heated in the electric furnace. The following reactions take place [1] :—

$$BaSO_4 + 4C = BaS + 4CO$$
$$BaS + 3BaSO_4 = 4BaO + 4SO_2.$$
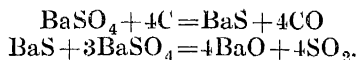
By heating barium chloride with zinc oxide at white heat, zinc chloride is made to volatilise and barium oxide is left.[2]

Barium hydroxide may be prepared electrolytically[3] and then converted into the oxide.

As ordinarily produced, it is a white (or often greyish) amorphous powder, the density of which varies considerably, from 4·73–5·76, with the method of production.[4] It may be obtained in a crystalline form by slow calcination of the nitrate, but, owing probably to the fact that, unlike calcium and strontium oxides, barium oxide does not dissolve in the nitrate, the crystals are only microscopic.[5] There are apparently two forms, cubic, of density 5·74, and hexagonal, of density 5·32.[5] By fusing in the electric furnace at a lower temperature than is possible in the case of calcium or strontium oxides, and allowing to cool, a crystalline mass is obtained.[6] Barium oxide also crystallises out when a mixture of barium and lithium carbonates is heated to 1150°–1250° C.[7]

The heat of formation of barium oxide is 125·86 Cal.[8]

Hydrochloric acid reacts with barium oxide even at ordinary temperatures, probably owing to the difficulty of making it completely anhydrous.[9] Sulphuretted hydrogen[10] and sulphur dioxide[11] only react when heated. By heating with carbon dioxide the reaction is so vigorous that the product becomes incandescent and may reach a temperature of 1200° C.[12] A basic carbonate of indefinite composition results.[13]

Investigations of the temperature of dehydration of hydrated barium hydroxide have led de Forcrand to the conclusion that barium oxide should be represented as a condensed product, $(BaO)_n$.[14]

In the presence of small quantities of phosphorogens, barium oxide is phosphorescent.[15]

Barium oxide dissolves in fused barium chloride to the extent of one molecule of oxide to one of chloride. Mixed crystals containing 17·7 per cent. of oxide separate out.[16]

[1] Bradley and Jacobs, *Zeitsch. Elektrochem.*, 1900, 7, 425 ; Jacobs, *J. Soc. Chem. Ind.*, 1902, 21, 391.

[2] Heinz, *Chem. Zeit*, 1901, 25, 199 ; Heinz gives a critical review of a number of processes for the production of barium oxide. For further references see Terres and Brückner, *Zeitsch. Elektrochem.*, 1920, 26, 1.

[3] See Barium Hydroxide.

[4] Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 417 ; Clarke, *Constants of Nature*, Part I. (Macmillan & Co.), 1888, p. 42.

[5] Brügelmann, *Wied. Annalen*, 1877, 2, 466 ; 1878, 4, 277 ; *Zeitsch. anal. Chem.*, 1890, 29, 126 ; *Zeitsch. anorg. Chem.*, 1908, 59, 248.

[6] Moissan, *Compt. rend.*, 1892, 115, 1034 ; *Ann. Chim. Phys.*, 1895, [7], 4, 139.

[7] Lebeau, *Ann. Chim. Phys.*, 1905, [8], 6, 438.

[8] de Forcrand, *Compt. rend.*, 1911, 152, 27.

[9] Veley, *Proc. Chem. Soc.*, 1894, 10, 240 ; *Ber.*, 1896, 29, 580.

[10] Schumann. *Annalen*, 1877, 187, 311.

[11] Birnbaum and Wittich, *Ber.*, 1880, 13, 651.

[12] Raoult, *Compt. rend.*, 1881, 92, 1110.

[13] See also Scheibler, *Ber.*, 1886, 19, 1973.

[14] de Forcrand, *Compt. rend.*, 1908, 147, 165.

[15] Schmidt, *Ann. Physik*, 1920, [4], 63, 264.

[16] Arndt, *Ber.*, 1907, 40, 427.

Owing to its tendency to form barium peroxide, the oxide may be used as a reducing agent for organic compounds.[1]

Barium Hydroxide, Ba(OH)$_2$.—Barium oxide, like the other alkaline earth oxides, combines with water with considerable evolution of heat, forming powdered barium hydroxide. It may be obtained commercially from the sulphide by the action of metallic oxides, for example zinc, copper, and lead, in the presence of water,[2] by treatment with superheated steam,[3] or by oxidation of the warm solution by air in the presence of Weldon mud.[4] It may also be prepared from the carbonate by the action of superheated steam at red heat.[5] The electrolysis of barium chloride solution with a mercury cathode, by methods similar to those employed for the production of alkali hydroxides, gives barium hydroxide.[6] An electrolytic process has also been suggested for the preparation of barium hydroxide from barium sulphide. Barium hydroxide is formed at the anode through the interaction of hydroxyl ions with barium sulphide.[7] A method of preparation for commercial use by the hydrolysis of tribarium silicate, or, more probably, an intimate mixture of one molecule of metasilicate with three molecules of barium carbonate, previously obtained by the fusion of barium carbonate with silica, has been described.[8]

The heat of formation of barium hydroxide from the oxide and water is 24·24 Cal.[9] It is an amorphous white powder of density 4·495,[10] and it melts at 325° C.[9] A high temperature is required to dehydrate the hydroxide. The following values have been found for the vapour pressure at different temperatures [11] :—

Temperature, °C.	630	670	710	749	789	829	870	910	951	998
Pressure, mm. Hg	9·2	17·4	31·5	55	92	149	234	355	526	760

Under the influence of the cathode rays, barium hydroxide fluoresces a bright orange-yellow.[12]

The heat of solution of barium hydroxide is 11·40 Cal.[9] It is more soluble than either strontium or calcium hydroxide, and its solubility increases considerably with temperature. The solution is strongly basic. The following values for the solubility have been found [13] :—

Temperature, °C.	0	6	12	16	21	30	41	54	64	70	77	80
Grams hydroxide as BaO in 100 grams water	1·5	1·8	2·4	3·0	3·6	5·0	7·6	14·0	23·8	31·9	70·0	90·77

The densities of barium hydroxide solutions,[14] and the electrical

[1] Zerewitinoff and von Ostromisslensky, *Ber.*, 1911, **44**, 2402.

[2] Muller, *J. prakt Chem.*, 1861, [1], **82**, 52 ; Stahlschmidt, *Dingl. poly. J.*, 1841, **82**, 30 ; Tessié du Motay, *ibid.*, 1872, **206**, 333.

[3] Ziomezynski, *ibid.*, 1883, **248**, 249.

[4] Pattinson, *Ber.*, 1886, **19**, Ref., 124, 325, 516.

[5] Leplay, *Dingl. poly. J.*, 1884, **254**, 436.

[6] Fedotieff and Weizer, *Zeitsch. anorg. Chem.*, 1914, **86**, 325.

[7] Brochet and Ranson, *Compt. rend.*, 1903, **136**, 1195, 1258 ; Marino and Gigli, *Gazzetta*, 1913, **43**, ii, 1.

[8] Deguide and Baud, *Compt. rend.*, 1922, **174**, 1177.

[9] de Forcrand, *ibid.*, 1908, **147**, 165.

[10] Filhol, *Ann. Chim. Phys.*, 1847, [3], **21**, 417.

[11] Johnston, *Zeitsch. physikal. Chem.*, 1908, **62**, 330 ; see also *J. Amer. Chem. Soc.*, 1908, **30**, 1357.

[12] Crookes, *Proc. Roy. Soc.*, 1881, **32**, 206.

[13] Rosensthiel and Ruhlmann, *Jahresber.*, 1870, 314.

[14] Kohlrausch, *Wied. Annalen*, 1879, **6**, 22.

conductivities of dilute solutions.[1] and of concentrated.[2] have been determined.

The solubility is considerably diminished by alkali hydroxides, and to a less extent by ammonia. It is also decreased by barium chloride, but increased by barium nitrate, probably through the formation of a complex ion.[3] Acetone [4] and alcohol [5] decrease the solubility.

On electrolysing a barium hydroxide solution, less oxygen is evolved than is equivalent to the hydrogen formed, probably owing to the production of barium peroxide or hydrogen peroxide.[6]

Carbon disulphide reacts with barium hydroxide solution at 100° C., forming barium carbonate and hydrosulphide.[7]

Hydrates of Barium Hydroxide.—Several hydrates of barium hydroxide have been described, but the existence of these has not in all cases been confirmed. At low temperatures Artus obtained the hydrate $Ba(OH)_2.16H_2O$.[8] From solutions at ordinary temperatures the octahydrate crystallises out.[9] The formulæ, $Ba(OH)_2.7H_2O$ [10] and $Ba(OH)_2.9H_2O$,[11] have also been assigned to the compound thus obtained.

The octahydrate may form monoclinic or tetragonal crystals, the latter being isomorphous with the corresponding strontium compound.[12] The density is 1 656,[13] and the heat of solution -14.5 Cal.[14] At 78° C. it melts in its water of crystallisation, and if the temperature be raised it boils at 103° C. As the water evaporates, the boiling-point rises to 109° C., at which temperature it remains constant, whilst large brilliant rhombic crystals of the trihydrate separate out.[15] From vapour pressure measurements, Lescœur concluded that a compound, $3Ba(OH)_2.10H_2O$, probably existed.[16] This is no doubt the trihydrate. The lustre rapidly disappears on exposure to air, and in dry air the crystals effloresce, forming the monohydrate. By heating the solution in equilibrium with the trihydrate to a still higher temperature, a white crystalline powder of the monohydrate is formed.[12] The latter is also obtained from the octahydrate by drying *in vacuo* or by heating for some time in a current of hydrogen at 45° C.,[14] or at 80° C.[17] The heat of solution is 7·06 Cal.[14] The monohydrate is changed to the hydroxide by heating in a current of hydrogen above 90°–95° C.[18]

[1] Ostwald, *J. prakt. Chem.*, 1886, [2], 33, 357.
[2] Kohlrausch, *Wied. Annalen*, 1879, 6, 22.
[3] Parsons and Corson, *J. Amer. Chem. Soc.*, 1910, 32, 1383; Harkins, *ibid.*, 1911, 33, 1857.
[4] Herz and Knoch, *Zeitsch. anorg. Chem.*, 1904, 41, 315.
[5] Beckmann, *J. prakt. Chem.*, 1883, [2], 27, 138.
[6] Duter, *Compt. rend.*, 1887, 104, 354.
[7] Chancel and Parmentier, *ibid.*, 1884, 99, 892.
[8] See Bauer, *Zeitsch. anorg. Chem.*, 1905, 47, 401 ; see also Johnston, *Zeitsch physikal. Chem.*, 1908, 62, 343.
[9] Beckmann, *loc. cit.*; Bloxam, *Jahresber.*, 1859, 131 ; Lescœur, *Ann. Chim. Phys.*, 1890, [6], 19, 59.
[10] Müller-Erzbach, *Ber.*, 1887, 20, 1628 ; 1889, 22, 3181 ; Filhol, *J. Pharm. Chim.*, 1845, [3], 7, 271.
[11] Berthelot, *Jahresber.*, 1873, 79 ; André, *Compt. rend.*, 1881, 93, 58 ; see Beckmann, *loc. cit.*
[12] Bauer, *loc. cit.*
[13] Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415
[14] de Forcrand, *loc. cit.*
[15] Bauer, *loc. cit.* ; *Zeitsch. angew. Chem.*, 1903, 16, 34
[16] Lescœur, *Compt. rend.*, 1883, 96, 1578.
[17] Veley, *Trans. Chem. Soc.*, 1886, 49, 371.
[18] de Forcrand, *loc. cit.* ; see also Lescœur, *loc. cit.*

The monohydrate will combine with carbon dioxide at fairly low temperatures, but a slight excess of water is apparently necessary.[1]

From vapour pressure measurements Muller-Erzbach concluded that a dihydrate can exist at 15° C.[2]

Barium oxide forms compounds with methyl[3] and ethyl[4] alcohol, and also with other alcohols, such as glycerol and mannitol.[5] According to de Forcrand these are not true alcoholates, but addition compounds, for example, $3BaO.4CH_3OH$ and $3BaO.4C_2H_5OH$.[6] In aqueous methyl alcohol a hydrated compound is formed.[7]

If ethyl alcohol and a little water be added to a methyl alcoholic solution of barium oxide, and the solution be slowly evaporated *in vacuo*, a compound, $Ba(OCH_3)_2$, separates out in transparent needles. It is soluble in water, slightly soluble in ethyl alcohol, and insoluble in ether or acetone.[8]

Uses of Barium Hydroxide.—Barium hydroxide was formerly used in the beet and cane sugar industries for separating otherwise un-crystallisable sugars by precipitating the sucrate and then decomposing it by carbon dioxide, but this process has now been abandoned.[9]

It is also used as a depilatory in tanning, in the white pigment and dry colour trades for the manufacture of permanent white for example, and for the softening of water for industrial purposes.[10]

Barium Peroxide, BaO_2.—Thénard observed that barium oxide absorbs oxygen probably equal in amount to that which is already present, and forms a peroxide.[11] The rate of reaction is practically zero at ordinary temperatures, but reaches an appreciable velocity above 400° C. At the same time, however, since combination with oxygen is accompanied by an evolution of 12·1 Cal. per gram-molecule,[12] the tendency to dissociate again into barium oxide and oxygen is in-creased, and an increased pressure of oxygen is, therefore, necessary to bring about complete transformation into peroxide. Thus, by heating the oxide alternately at a lower temperature, and then at a higher one, in air, it was found possible to use it as a means of separating oxygen from the air. It was observed that the reactants must not be absolutely anhydrous, but that at the same time the amount of water present must be small.[13] The process was modified by Brin, who kept the temperature constant and alternately raised and lowered the pressure.[14] The air had to be previously purified from carbon dioxide and organic matter, and

[1] Beckmann, *loc. cit.*; Scheibler, *Ber.*, 1886, 19, 1973.
[2] Muller-Erzbach, *loc. cit.*
[3] Dumas and Péligot, *Ann. Chim Phys.*, 1835, [2], 58, 17; de Forcrand, *Compt. rend.*, 1886, 102, 1397, 1557.
[4] Berthelot, *Ann. Chim. Phys.*, 1856, [3], 46, 180; de Forcrand, *Compt. rend.*, 1883, 97, 170; Destrem, *Ann. Chim. Phys.*, 1882, [5], 27, 7.
[5] Ubaldini, *Ann. Chim. Phys.*, 1859, [3], 57, 213.
[6] de Forcrand, *Compt. rend*, 1895, 120, 737.
[7] de Forcrand, *ibid.*, 1886, 103, 59.
[8] Neuberg and Neimann, *Biochem. Zeitsch.*, 1906, 1, 166.
[9] Heriot, *The Manufacture of Sugar from the Cane and Beet* (Longmans, Green & Co.), 1920 (Monographs on Industrial Chemistry), p. 336.
[10] Jacobs, *J. Soc. Chem. Ind.*, 1902, 21, 391; see also Hundeshagen, *ibid.*, 1918, 37, 670A.
[11] Thénard, *Ann. Chim. Phys.*, 1818, [2], 8, 306; Rammelsberg, *Pogg. Annalen*, 1838, 44, 588; Boussingault, *Ann. Chim. Phys.*, 1852, [3], 35, 5.
[12] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 6, 209; de Forcrand, *Compt. rend.*, 1900, 130, 1017.
[13] Boussingault, *loc. cit.*
[14] L. Q. and A. Brin, English Patents, 1416 (1880); 151, 157 (1885); see also *J. Soc. Chem. Ind.*, 1885, 4, 568.

a porous oxide was necessary. Brin's process for obtaining oxygen has now been superseded by air-fractionation methods.

Recent work on the catalytic acceleration of the reaction by various oxides, for example copper, zinc, cadmium, magnesium, calcium, silicon, antimony, bismuth, uranium, tungsten, and molybdenum oxides,[1] has suggested the possible revival of the Brin process under more favourable conditions of temperature.[2] Some of the oxides mentioned form stable salts with barium, and would, therefore, be unsuitable for commercial purposes, as they would no doubt soon put the barium oxide out of action.

Barium peroxide is a white powder, stable under ordinary conditions if anhydrous, and protected from carbon dioxide.[3] It melts at bright red heat with the evolution of oxygen.[4] When heated with hydrogen, water, sulphur, carbon, carbon monoxide, sulphur dioxide, or ammonia, it is reduced.[5] By heating with chlorine,[6] or iodine,[7] the oxygen is replaced by the halogen. With concentrated sulphuric acid at ordinary temperatures ozonised oxygen is given off.[8] With dilute hydrochloric acid, hydrogen peroxide is formed, and oxygen with concentrated. Potassium ferricyanide is reduced by barium peroxide, forming a double potassium barium ferrocyanide and free oxygen, and this reaction may be used as a means of estimating barium peroxide.[9] With formaldehyde, barium formate and hydrogen are produced.[10] By heating to redness with precipitated metallic gold a bright green mass is obtained which, on treatment with water, gives a solution of barium aurate, $Ba(AuO_2)_2$.[11]

The dissociation pressures of barium peroxide for different temperatures were first investigated by Le Chatelier.[12] The difficulty of the determinations is much enhanced by the fact that a solid solution of barium oxide and peroxide is formed, so that the pressure at any one temperature will be influenced by the proportions of these two present, and, further, by the necessity for the presence of water vapour.[13] The dissociation has, however, been carefully studied by Hildebrand.[14] As already stated, a small amount of water is necessary as a catalyst. After some of the peroxide has been decomposed, barium hydroxide will therefore be present. Experiments on the vapour pressure of barium hydroxide do not indicate the formation of a solid solution with the oxide,[15] and the same is probably true of the peroxide and hydroxide.

Starting from the peroxide, the system is at first divariant. There are three components, water, barium oxide, and oxygen; and three phases, barium hydroxide, an unsaturated solid solution of barium oxide in barium peroxide, and the gaseous phase composed of oxygen and water vapour. Therefore there are two degrees of freedom. At any one

[1] Hedvall, *Zeitsch. anorg. Chem.*, 1918, 104, 163; Hedvall and von Zweibergk, *ibid.*, 1919, 108, 119.

[2] Kendall and Fuchs, *J. Amer. Chem. Soc.*, 1921, 43, 2017.

[3] Berthelot, *Ann. Chim. Phys.*, 1878, [5], 14, 433.

[4] Schöne, *Ber.*, 1873, 6, 1172.

[5] Wöhler, *Annalen*, 1851, 78, 125; Boussingault, *loc. cit.*; Michel and Grandmougin, *Ber.*, 1893, 26, 2567; Schillbach, *Zeitsch. angew. Chem.*, 1903, 16, 1080.

[6] Baudrimont, *Compt. rend.*, 1866, 62, 829.

[7] Bodroux, *ibid.*, 1906, 142, 279.

[8] Houzeau, *Ann. Chim. Phys.*, 1861, [3], 62, 129.

[9] Kassner, *Arch. Pharm.*, 1890, 228, 432.

[10] Lyford, *J. Amer. Chem. Soc*, 1907, 29, 1227.

[11] Meyer, *Compt. rend.*, 1907, 145, 805.

[12] Le Chatelier, *ibid.*, 1892, 115, 654.

[13] Boussingault, *loc. cit.*   [14] Hildebrand, *J. Amer. Chem. Soc.*, 1912, 34, 246.

[15] Johnston, *Zeitsch. physikal. Chem.*, 1908, 62, 330.

temperature the oxygen pressure will vary with the concentration of the solid solution, which will depend on the proportion of barium peroxide decomposed. When about one-third of the peroxide has been decomposed the barium peroxide is saturated with barium oxide, and the system becomes monovariant owing to the appearance of a second solid solution of the two, thus making a fourth phase. The composition of the two saturated solid solutions may vary slightly with varying temperature, but at constant temperature will remain constant, although the amount of the second solution will increase at the expense of the first as the proportion of barium peroxide is diminished. The point at which the system becomes monovariant depends on the amount of water present, and hence on the amount of barium hydroxide which will be formed. The system again becomes divariant when about 98 per cent. of the peroxide has been decomposed.

The conditions necessary to produce 100 per cent. barium peroxide from barium oxide were studied. Oxygen of definite moisture content, which was less than the vapour pressure of barium hydroxide at the temperature under consideration, was passed, under slightly more than one atmosphere pressure, over barium oxide heated to a definite temperature in an electric oven. Successive equal samples were acted upon for equal times and the product analysed. Similar experiments were carried out with air. The following results were obtained :—

Temperature, °C.	200	300	350	400	500	600	700	750	800	900
Percentage BaO_2, using oxygen.	3·7	17·3	71·1	96·4	100	100	96·9	61·9	18·2	0·9
Percentage BaO_2, using air	..	18·2	..	70·4	69·2	52 8	30·9	.	5·9	..

With sufficient water present to give the vapour pressure of barium hydroxide, and sufficient barium oxide to produce the monovariant system, the following values for the pressure were obtained and compared with the values calculated from the equation

$$\log_{10}p = -6850/T + 1·75 \log_{10}T + 3·807,$$

where T is the absolute temperature and p is expressed in mm.

Temp., °C.	Pressure in mm. mercury.			
	Observed.	Calculated.[1]	Aqueous Pressure.	Oxygen Pressure.
540	2	2·98	..	..
618	18	19·1	7·3	11·3
655	41	41·4	13·7	26 8
697	91	93·6	26·3	65·4
737	193	191	47	141
794	479	483	98	378
835	871	893	139	718
853	1128	1156	195	937
868	1401	1426	231	1160

[1] These have been recalculated from Hildebrand's formula; there is apparently an error in the original calculations.

These are all lower than Le Chatelier's values. The heat of combination of barium oxide and oxygen calculated from these results is 18·71 Cal. per gram-molecule of peroxide. The disagreement with Berthelot's value, 12·1 Cal., seems too large to be accounted for by the formation of solid solutions.

Hydrates of Barium Peroxide.—Anhydrous barium peroxide combines with water with the evolution of 9·1 Cal. of heat per gram-molecule.[1] The octahydrate, $BaO_2.8H_2O$, in pearly plates, is formed,[2] but the formulæ $BaO_2.10H_2O$ and $7H_2O$ have also been assigned to it.[3]

When barium peroxide is obtained by precipitation of barium hydroxide solution with hydrogen peroxide, the octahydrate is always formed at ordinary temperatures if less than one molecule of hydrogen peroxide be present per molecule of hydroxide, and above 60° C. whatever the composition of the solution.[4] Jaubert patented a process for obtaining hydrated barium peroxide by lixiviating barium sulphide with boiling water, cooling to 25°–30° C., and adding sodium peroxide in cold water. The barium peroxide separates out in scales which may be filtered, washed, and pressed.[5]

The octahydrate effloresces on exposure to air, and carbonate is also formed.[6]

Berthelot mentions a monohydrate, heat of hydration 1·4 Cal.,[7] but it is probably the peroxyhydrate.

Barium peroxide may be estimated iodometrically by adding potassium iodide to a hydrochloric acid solution of the compound and titrating the liberated iodine with thiosulphate,[8] or by titrating with permanganate a hydrochloric acid solution to which a considerable quantity of manganous sulphate solution has afterwards been added.[9] A sulphuric acid solution cannot be employed, because the precipitated sulphate carries with it a large quantity of peroxide which escapes reaction.[10]

Barium peroxide may be used for bleaching purposes, but its chief use is in the production of hydrogen peroxide by decomposition with an acid.

Barium Peroxyhydrate.—By the action of hydrogen peroxide on the crystallised peroxide, or of more than one equivalent of hydrogen peroxide on barium hydroxide, or of hydrogen peroxide and ammonia on a barium salt, between 30° and 60° C., barium monoperoxyhydrate, $BaO_2.H_2O_2$, is obtained in monoclinic crystals.[11] At room temperature it soon becomes yellow without evolution of oxygen. Then oxygen begins to escape, and after four or five days, when half the available

[1] Berthelot, *Ann. Chim. Phys.*, 1880, [5], **21**, 154.

[2] Schöne, *Ber.*, 1873, 6, 1172 ; Schöne and Grigorieff, *Bull. Soc. chim.*, 1881, [2], **35**, 107.

[3] Berthelot, *Ann. Chim Phys.*, 1878, [5], **14**, 433 ; 1880, [5], **21**, 154, 159.

[4] Riesenfeld and Nottebohm, *Zeitsch. anorg. Chem.*, 1914, **89**, 405 ; see also Thénard, *Ann. Chim. Phys.*, 1818, [2], 8, 312.

[5] Jaubert, *J. Soc. Chem. Ind.*, 1901, **20**, 42, 474.

[6] Schöne, *loc. cit.*

[7] Berthelot, *Ann. Chim. Phys.*, 1880, [5], **21**, 158.

[8] Bertrand, *Bull. Soc. chim.*, 1880, [2], **33**, 148.

[9] See Volumetric Estimation of Calcium.

[10] Löb, *Chem. Zeit.*, 1906, **30**, 1275

[11] Riesenfeld and Nottebohm, *loc. cit.* ; see also Schöne, *Ber.*, 1873, 6, 1172 ; *Annalen*, 1878, **192**, 264.

oxygen has gone, the yellow colour disappears. At 50°–60° C. decomposition takes place in a few minutes. The reaction is probably as follows, with the possible intermediate formation of a monohydrate :—

$$2BaO_2.H_2O_2 = 2BaO_2 + 2H_2O + O_2.$$

The heat of formation from barium peroxide and hydrogen peroxide is 5 1 Cal.[1] De Forcrand supposed the compound to have the structural

formula $Ba\begin{cases} O-OH \\ O-OH \end{cases}$.[2]
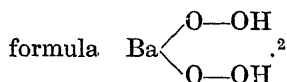
By the action of an excess of hydrogen peroxide on a cooled barium salt solution and precipitation by ammonia, a diperoxyhydrate, $BaO_2.2H_2O_2$, is obtained.[3]

Barium Tetroxide, BaO_4.—Schöne suggested that the yellow compound, which is obtained from the monoperoxyhydrate without change of composition, probably represents a higher state of oxidation than the peroxide.[4] Traube and Schulze regard it as a tetroxide, and, as in the case of the calcium tetroxide, suppose it to be comparable with the polysulphides, thus writing its formula as $BaO_2.O_2$.[5] They never obtained samples containing more than 8 per cent. of tetroxide, but these were of a rather intense yellow, indicating that the pure substance would probably be very dark. A fairly high temperature is necessary to destroy the colour completely. As in the case of calcium tetroxide, no other means of oxidation than hydrogen peroxide can be used.

BARIUM AND SULPHUR.

Barium Sulphide, BaS, may be formed by the action of sulphuretted hydrogen on the hydroxide at 85° C., with subsequent heating in hydrogen at 200° C.,[6] on barium carbonate at red heat, or, finally, on the sulphate at 1200° C., in all three cases cooling in hydrogen.[7] It may also be obtained by the action of carbon disulphide on barium carbonate.[8]

$$BaCO_3 + 2CS_2 = BaS + 3CO + 3S.$$

Polysulphides are always formed in this case, but may be reduced to the sulphide by heating in a current of hydrogen.

The method employed for the technical production of barium sulphide is the reduction of barytes by carbon or reducing gases. The sulphide thus formed is the starting-point for the production of all other commercial barium compounds. Laboratory tests indicate that a high temperature for a short time produces a more satisfactory yield than a

[1] Berthelot, *Ann. Chim. Phys*, 1880, [5], **21**, 153 ; see also de Forcrand, *Compt. rend.*, 1900, **130**, 778, 834.

[2] de Forcrand, *ibid.*, 716.

[3] Riesenfeld and Nottebohm, *loc. cit.*

[4] Schöne, *Annalen*, 1878, **192**, 283 ; see also Rammelsberg, *Ber.*, 1874, **7**, 542 ; de Forcrand, *Compt. rend.*, 1900, **130**, 834.

[5] Traube and Schulze, *Ber.*, 1921, **54B**, 1633.

[6] Veley, *Trans. Chem. Soc.*, 1886, **49**, 369.

[7] Sabatier, *Ann. Chim. Phys.*, 1881, [5], **22**, 6.

[8] Schöne, *Pogg. Annalen*, 1861, **112**, 193.

low temperature with prolonged heating.[1] Good results are obtained with 15–16 per cent. of carbon in muffles at $1000°$–$1100°$ C.[1]

Barium sulphide as usually obtained is a greyish white amorphous powder, but after fusion in the electric furnace it forms cubic crystals of density 4 25.[2] The heat of formation is 105 2 Cal.[3]

On exposure to air it turns yellow. It is not reduced by hydrogen at $1200°$ C., but is readily attacked by halogens and is completely transformed into the sulphate by oxygen at high temperatures. It is attacked by gaseous acids in the cold. Carbon decomposes it at the temperature of the electric arc forming the carbide.[4] Oxidising agents react with incandescence. When it is heated in water vapour, hydrogen and barium sulphate are formed.[5] It is attacked by concentrated nitric acid with incandescence, and reacts with phosphorus trichloride forming barium chloride and phosphorus trisulphide.[6] On heating with an equal quantity of barium chloride it forms an opaque red mass.[7] In general, the crystallised sulphide is less readily attacked than the amorphous.[2]

Barium sulphide is readily soluble in water with hydrolysis, forming the hydroxide and hydrosulphide.[8] The heat of solution is 7 3 Cal.[3] If the aqueous solution be concentrated *in vacuo* in the presence of free sulphur, a hydrated sulphide, $BaS.6H_2O$, crystallising in hexagonal plates, is obtained.[9] When slowly heated it loses water between $100°$ and $300°$ C., and then sulphuretted hydrogen and sulphur.

It is insoluble in alcohol.

A dark red double barium nickel sulphide, $BaS.4NiS$ has been obtained.[10]

Phosphorescent Barium Sulphide.—Barium sulphide, under the name of Bolognian phosphorus,[11] was the first of the alkaline earth sulphides in which the property of phosphorescence was observed. The conditions affecting the phosphorescence of these sulphides have already been discussed under calcium sulphide.

Barium Hydrosulphide, $Ba(SH)_2$, is formed by passing sulphuretted hydrogen into a saturated barium hydroxide solution at $60°$–$70°$ C., and then cooling,[12] or by dissolving barium sulphide in sulphuretted hydrogen water. By evaporation of the solution *in vacuo* in the cold, or by precipitation with alcohol, white, opaque, needle-shaped crystals are obtained containing 4 molecules of water, $Ba(SH)_2.4H_2O$.[13] When heated in hydrogen they lose water and a little sulphuretted hydrogen above $55°$ C., but when the substance is dehydrated its stability is increased. It is only at red heat

[1] Wells, *J. Ind. Eng. Chem.*, 1916, 8, 770 ; see also Mourlot, *Ann. Chim. Phys.*, 1899, [7], 17, 517.
[2] Mourlot, *loc. cit.* ; *Compt. rend.*, 1898, 126, 643.
[3] de Forcrand, *Ann. Chim. Phys.*, 1911, [8], 24, 272.
[4] Mourlot, *loc. cit.* ; Gay-Lussac, *Ann. Chim.*, 1813, [1], 85, 199.
[5] Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 386 ; Louth, *Bull. Soc. chim*, 1866, [2], 5, 249.
[6] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 20.
[7] Berthier, *ibid.*, 1830, [2], 43, 310.
[8] Rose, *Pogg. Annalen*, 1842, 55, 415.
[9] Schöne, *Pogg. Annalen*, 1861, 112, 193.
[10] Bellucci and Bellucci, *Atti R. Accad. Lincei*, 1908, [5], 17, i, 18.
[11] See History.
[12] Veley, *Trans. Chem. Soc.*, 1886, 49, 375 ; Fischer and Raske, *Ber.*, 1908, 41, 894.
[13] Rose, *loc. cit.* ; see also Berthollet, *Ann. Chim.*, 1798, [1], 25, 241.

that sulphuretted hydrogen is completely eliminated and barium sulphide formed.

Solutions of barium hydrosulphide have a considerable partial pressure of sulphuretted hydrogen. Determinations of the solubility in water between $-15°$ C. and $100°$ C. have been made in closed tubes to prevent the escape of sulphuretted hydrogen.[1]

Temperature, °C.			-15	0	20	40	60	80	100
Grams $Ba(SH)_2$ per 100 grams solution			32	32·6	32·8	34·5	36·2	39·0	43·7

Barium Polysulphides.—*Barium Trisulphide*, BaS_3. is obtained by heating barium sulphide with excess of sulphur at a temperature not greater than $360°$ C.[2] It forms a yellowish-green mass, fusible at $400°$ C., above which temperature it loses sulphur, but it is only completely transformed into the monosulphide at dull red heat. In warm water it partially dissolves, forming a reddish-yellow solution which has an alkaline reaction and is readily oxidised in air.[2]

Barium Tetrasulphide, BaS_4.—By boiling a mixture of barium sulphide and sulphur with water,[2] or by treating sulphur with a saturated solution of barium hydrosulphide,[3] and evaporating, red crystals of composition $BaS_4.H_2O$ or $2H_2O$ separate in the form of rhombic prisms of density 3. By boiling a mixture of barium hydroxide, sulphur, and water a deep brown liquid is obtained which becomes orange-red on cooling. By rapid evaporation, red crystals of $BaS_4.H_2O$, mixed with sulphur and barium thiosulphate, are formed. The mother liquor contains barium and sulphur in the proportion BaS_5, but this compound is probably not obtained in the solid state,[4] the solution depositing the tetrasulphide and free sulphur.

The tetrasulphide is more stable than the trisulphide. When heated, it loses sulphur at about $110°$ C., and water and sulphuretted hydrogen above $200°$ C. At $300°$ C. it is decomposed into the trisulphide and sulphate. It dissolves in water to the extent of one part in 2·53 of water at $15°$ C., without decomposition, forming a red solution from which the tetrasulphide can be recrystallised. The solution is not decomposed by sulphuretted hydrogen.[3]

By evaporating a solution of the trisulphide, Schöne obtained orange-red monoclinic crystals showing dichroism, of composition $Ba_4S_7.25H_2O$, or $24H_2O$,[5] but he expressed doubt as to whether it was a chemical individual or an isomorphous mixture of the mono- and tetra-sulphides.

No higher polysulphide appears to have been obtained.

Barium Hydroxyhydrosulphide.—By extracting barium sulphide with water a solution containing equal molecular quantities of the hydroxide and hydrosulphide is obtained. This is probably a solution of a double compound, $Ba(OH)_2.Ba(SH)_2$, or a hydroxyhydrosulphide, $Ba(OH)(SH)$. By mixing concentrated solutions of the two constituents a compound is precipitated of composition $Ba(OH)_2.Ba(SH)_2.10H_2O$, or, regarded as a hydroxyhydrosulphide, $Ba(OH)(SH).5H_2O$. The

[1] Terres and Brückner, *Zeitsch. Elektrochem.*, 1920, **26**, 13.
[2] Schöne, *Pogg. Annalen*, 1861, **112**, 193.
[3] Veley, *Trans. Chem. Soc.*, 1886, **49**, 369.
[4] Guiteau, *Compt. rend.*, 1916, **163**, 390.
[5] See Geuther, *Annalen*, 1884, **224**, 200.

maximum yield is obtained when about thirty molecules of the hydrosulphide are present to one of the hydroxide.[1] The pressure of sulphuretted hydrogen over this compound is very small compared with that over the hydrosulphide.

The hydroxyhydrosulphide may also be formed by the incomplete saturation of barium hydroxide with sulphuretted hydrogen, by passing hydrogen through a solution of the hydrosulphide, or by the action of sodium hydroxide on barium hydrosulphide or sulphide. It is evident that the latter cannot be used as a method for the preparation of barium hydroxide. Pure barium hydroxide can never be crystallised from solutions obtained by the action of water on barium sulphide.[1]

The composition of solutions in equilibrium with the hydroxy-hydrosulphide at different temperatures has been determined.[1]

Barium Oxysulphides.—A solution of barium sulphide kept for a long time protected from the air deposits oxysulphides of variable composition.[2] By the action of sulphuretted hydrogen on barium oxide a compound or mixture of composition $3BaS.BaO$ is obtained.[3]

Barium Sulphite, $BaSO_3$, is precipitated by the action of an alkali sulphite on a solution of a soluble barium salt.[4] It is also formed by the action of sulphur dioxide on a suspension of barium hydroxide or carbonate, or of sulphur dioxide on barium oxide at 200°–230° C.[5] It dissolves in sulphurous acid, from which it may be recrystallised in colourless hexagonal prisms.[6] By heating the anhydrous salt it is decomposed into the sulphide and sulphate.[7]

The solubility in water is very small and diminishes with rise of temperature, 0·01974 grm. dissolving in 100 grm. of water at 20° C., and 0·00177 at 80° C. The solubility is decreased by cane sugar at the lower temperature, but at the higher temperature it is at first increased, and then, with increasing concentration of sugar, it is decreased.[8]

Barium sulphite is soluble in most acids.

Barium Thiosulphate, BaS_2O_3, is prepared by mixing hot concentrated solutions of barium chloride and sodium thiosulphate and allowing to cool.[9] It forms brilliant white crystalline plates of a silvery appearance containing 1 molecule of water, which is lost at 100° C.[10] It has a specific heat of 0·163 [11] and a density of 3·45 at 18° C.[12] When heated out of contact with air it is decomposed into a mixture of sulphate, sulphite, and sulphide.[13] It is only slightly soluble in water and practically insoluble in alcohol. It may be used instead of the sodium salt for iodine titrations.[14]

[1] Terres and Bruckner, *Zeitsch. Elektrochem.*, 1920, **26**, 14.
[2] Rose, *Pogg. Annalen*, 1842, **55**, 415.
[3] Schumann, *Annalen*, 1877, **187**, 311.
[4] Fourcroy and Vauquelin, *Ann. Chim.*, 1797, [1], **24**, 250 ; Muspratt, *Annalen*, 1844, **50**, 273 ; Rohrig, *J. prakt. Chem*, 1888, [2], **37**, 232.
[5] Birnbaum and Wittich, *Ber.*, 1880, **13**, 651.
[6] Röhrig, *loc. cit.* ; see also Muspratt, *loc. cit.*
[7] Forster, *Pogg. Annalen*, 1868, **133**, 94, 228 ; Mourelo, *Compt. rend.*, 1898, **126**, 420.
[8] Rogowicz, *Zeitsch. Ver. Deut. Zucker-Ind.*, 1905, **596**, 938 ; Weisberg, *Bull. de l'Assoc. de Sucre.* 1897, **4**, 560.
[9] Forster, *loc. cit.* ; Mutmanski, *Zeitsch. anal. Chem.*, 1897, **36**, 220.
[10] Letts, *J. Chem. Soc.*, 1870, **23**, 427.
[11] von Pape, *Pogg. Annalen*, 1864, **122**, 410.
[12] Clarke, *Jahresber.*, 1877, 43.
[13] Rammelsberg, *Pogg. Annalen*, 1842, **56**, 295 ; Rose, *ibid.*, 1831, **21**, 440.
[14] Plimpton and Chorley, *Trans. Chem. Soc.*, 1895, **67**, 314.

A double salt with bismuth, $Ba_3[Bi(S_2O_3)_3]_2$, regarded as containing a complex anion, has been described.[1]

Barium Dithionate, BaS_2O_4, may be obtained by neutralising barium hydroxide with dithionic acid, or by the interaction of manganese dithionate with barium hydroxide or sulphite. It crystallises with 2 molecules of water[2] in hexagonal plates stable in air,[3] or with 4 molecules in crystals similar to heavy spar,[4] of density 3·06 at 24·5° C.[5] It is very soluble, one part dissolving in four parts of water at 18° C., and in 1·1 parts at 100° C., forming a solution stable at ordinary temperatures. It is insoluble in alcohol. When heated it decomposes into water, sulphur dioxide, and barium sulphate.[3] Sodium amalgam, and also zinc and hydrochloric acid, reduce it to the sulphite.[6]

It forms a double salt with barium chloride, $BaS_2O_6.BaCl_2.4H_2O$.[2]

Barium Trithionate, BaS_3O_6, is obtained by neutralising trithionic acid with barium carbonate[7] and precipitating by alcohol. It forms glistening leaflets of composition $BaS_2O_6.2H_2O$.[8] A little is also formed by the action of sulphur chloride on barium sulphite in suspension in water.[9]

The aqueous solution readily decomposes when heated, forming barium sulphate.[10]

Barium Tetrathionate, BaS_4O_6, is obtained in fine needle-shaped crystals, containing 2[11] or 3[12] molecules of water of crystallisation, by the action of tetrathionic acid on an equivalent quantity of barium acetate and precipitation with absolute alcohol.[7] It is also formed by the action of sulphur dichloride on sulphurous acid, removal of the chloride and sulphate by lead, saturation with barium hydroxide, and precipitation by alcohol.[11] The crystals lose 1 molecule of water *in vacuo*.[13] When iodine acts upon barium thiosulphate in the presence of a little water, or when barium pentathionate spontaneously decomposes, the tetrathionate is formed.

It is decomposed at 100°–110° C., forming barium sulphate, sulphur dioxide, and sulphur. The aqueous solution is stable,[14] but the alcoholic solution is rapidly decomposed if acid be present, giving barium thiosulphate.

Barium Pentathionate, BaS_5O_6, is prepared by the neutralisation of pentathionic acid by barium carbonate, and precipitation by alcohol,[15] or by the action of sulphur chloride on barium thiosulphate.[9] It forms small oblong rectangular plates with a truncated corner, containing 2[16]

[1] Hauser, *Zeitsch. anorg. Chem.*, 1903, **35**, 9.
[2] Fock and Kluss, *Ber.*, 1890, **23**, 3001.
[3] Welter and Gay-Lussac, *Ann. Chim. Phys.*, 1819, [2], **10**, 314.
[4] Heeren, *Pogg. Annalen*, 1826, **7**, 172.
[5] Clarke, *Ber.*, 1879, **12**, 1398.
[6] Otto, *Annalen*, 1868, **147**, 187.
[7] Kessler, *Pogg. Annalen*, 1848, **74**, 274.
[8] Fordos and Gélis, *Ann. Chim. Phys.*, 1848, [3], **22**, 72.
[9] Spring, *Ber.*, 1873, **6**, 1108.
[10] See Pelouze, *Ann. Chim. Phys.*, 1842, [3], **4**, 85.
[11] Fordos and Gélis, *ibid.*, 1848, [3], **22**, 71.
[12] Lewes, *Trans. Chem. Soc.*, 1881, **39**, 72.
[13] Plessy, *Ann. Chim. Phys.*, 1847, [3], **20**, 162 ; Fordos and Gélis, *loc. cit.*
[14] Curtius and Henkel, *J. prakt. Chem.*, 1888, [2], **37**, 137 ; Lewes, *loc. cit.*
[15] Lenoir, *Annalen*, 1847, **62**, 253.
[16] Lenoir, *loc. cit.* ; Fordos and Gélis, *Ann. Chim. Phys.*, 1848, [3], **22**, 78.

or 3 [1] molecules of water. It is less stable than the tetrathionate. On being heated below 100° C., barium sulphate, sulphur, and sulphur dioxide are formed.[1] The water of hydration may be replaced by alcohol, the resulting compound being much more stable than the hydrated salt. Barium pentathionate is very soluble in water. When boiled, the solution gives sulphur dioxide. It is readily oxidised by chlorine.[2]

Barium Sulphate, BaSO$_4$, occurs naturally as the mineral *barytes* or *heavy spar*. It was the first known of the compounds of barium. It crystallises in the rhombic system and is usually white and opaque, but it sometimes forms transparent crystals which are colourless, or have brownish, greenish, or bluish shades. The finest specimens come from the Auvergne, Hungary, Bohemia, and Cumberland. A monoclinic form of the naturally occurring compound found in Quebec has been described.[3] The mineral *barytocelestine* is an isomorphous mixture of barium and strontium sulphates.[1] The water of a chalk well in Harrow has been found to contain barium sulphate.[5]

Barium sulphate may be prepared by the precipitation of a soluble barium salt with a soluble sulphate or sulphuric acid. There is no action if pure sulphuric acid be placed in contact with anhydrous barium oxide, a little water being necessary.[6] Spring obtained it by compressing a mixture of sodium sulphate and barium carbonate under 6000 atmospheres.[7]

The precipitated sulphate is amorphous, or composed of crystals of microscopic dimensions. Larger crystals may, however, be obtained by very slow precipitation in very dilute solutions; [8] by heating the precipitate in a sealed tube with hydrochloric acid or sodium bicarbonate at 250° C.; [9] by fusion of potassium sulphate with barium chloride,[10] of barium fluoride with calcium sulphate in presence of potassium chloride and sodium chloride,[11] or of barium sulphate with barium chloride at 1150 ° C., or with sodium sulphate at 1130° C., which is simply crystallisation from a solvent; [12] and, finally, by evaporation of a sulphuric acid solution of barium sulphate at, or a little below, the boiling-point.[13]

Manross found the density of the crystallised product to be 4·179.[14]

According to von Weimarn, a substance usually precipitated in the crystalline state may be obtained in the colloidal form under conditions which diminish the solubility and thus increase the number of centres of precipitation.[15] Barium sulphate may, therefore, be prepared in a colloidal form by precipitation from solutions containing methyl [16] or

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[1] Lewes, *Trans. Chem. Soc.*, 1881, **39**, 72.

[2] Fordos and Gélis, *loc. cit.*

[3] Lacroix, *Compt. rend.*, 1889, **108**, 1126; but see Dana, *Amer. J. Sci.*, 1890, [3], **39**, 61.

[4] Grahmann, *Jahrb Min.*, 1920, **1**, 1.

[5] Bloxam, *Chem. News*, 1884, **49**, 3.

[6] Kuhlmann, *Annalen*, 1838, **27**, 22.

[7] Spring, *Bull. Soc. chim.*, 1885, [2], **44**, 166; 1886, [2], **46**, 299.

[8] de Schulten, *Compt. rend.*, 1903, **136**, 1444.

[9] de Sénarmont, *Ann. Chim. Phys.*, 1851, [3], **32**, 155.

[10] Manross, *Annalen*, 1852, **82**, 349.

[11] Scheerer and Drechsel, *J. prakt. Chem*, 1873, [2], **7**, 68.

[12] Cooper and Fuller, *J. Amer. Chem. Soc.*, 1911, **33**, 845.

[13] Gaubert, *Compt. rend.*, 1907, **145**, 877.

[14] Manross, *loc. cit.*; see also Schröder, *Pogg. Annalen*, 1859, **106**, 226.

[15] von Weimarn, *Zeitsch. Chem. Ind. Koll.*, 1907, **2**, 76; 1908, **3**, 282; 1909, **4**, 27; see also *Chem. Zentr.*, 1910, i, 74.

[16] Neuberg and Neimann, *Biochem. Zeitsch.*, 1906, **1**, 166.

ethyl alcohol,[1] glycerol,[2] amyl alcohol,[3] or an alkaline solution of casein.[4] In the latter case crystallisation is probably prevented by the coating of the particles of barium sulphate with casein. Colloidal barium sulphate is also obtained by precipitating a very concentrated solution of barium acetate with aluminium sulphate,[5] or with magnesium or sodium sulphate.[6]

The melting-point of barium sulphate is 1580° C., at which temperature partial decomposition also takes place.[7] The specific heat increases linearly from 0·1137 at 150° C. to 0·1486 at 1050° C.[8]

There is apparently a transition point from β-$BaSO_4$ to α-$BaSO_4$ on heating above 1149° C. Strontium and barium sulphates are completely miscible in all proportions in both α- and β-forms; barium and calcium sulphates are isodimorphous, but the miscibility is at most 5 gram-molecules per cent. of calcium sulphate in barium sulphate.[9]

Barium sulphate alone does not fluoresce under the influence of the cathode rays, but will do so if a little bismuth be present.[10]

The effect of reducing agents on barium sulphate has already been described.[11] By fusion with alkali carbonates,[12] or boiling with solutions of the latter, it is transformed into the carbonate.[13] This reaction was Guldberg and Waage's classic example in their deduction of the law of mass action. When heated with ammonium chloride, barium chloride is formed.[14]

The solubility of barium sulphate in water is exceedingly small. From electrical conductivity determinations Kohlrausch found for precipitated barium sulphate 0·0197 milli-equivalents, or 2·30 mgm. per litre at 18° C., and 0·0226 milli-equivalents for the natural barytes.[15] The higher value for the latter may be due to impurities in the mineral. Melcher obtained the following values at different temperatures[16] :—

Temperature, °C. . .	18	25	50	100
Milli-equivalents per litre	0·0190	0·0212	0·0288	0·0334

By calculation from the change of solubility with temperature the

[1] Yogoro Kato, *Mem. Coll. Sci. Eng. Kyoto*, 1909–1910, 2, 187, see *J. Chem. Soc.*, 1910, 98, Abs. ii, 850.

[2] Recoura, *Compt. rend*, 1908, 146, 1274.

[3] von Weimarn, *Zeitsch Chem. Ind. Koll.*, 1908, 3, 89.

[4] Feilmann, *Trans. Faraday Soc.*, 1909, 4, 175.

[5] Buchner, *Chem. Zeit.*, 1893, 17, 878.

[6] Sacher, *ibid.*, 1911, 35, 1447.

[7] Doeltz and Mostowitsch, *Zeitsch. anorg. Chem.*, 1907, 54, 146 ; see also Boussingault, *Ann. Chim. Phys.*, 1867, [4], 12, 424. By extrapolation from the freezing-point curves of barium sulphate and sodium sulphate a melting-point 1345° C. is indicated, see Calcagni, *Atti R. Accad. Lincei*, 1912, [4], 21, i, 483.

[8] Laschtschenko, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 1604.

[9] Grahmann, *Jahrb. Min.*, 1920, 1, 1.

[10] de Boisbaudran, *Compt. rend.*, 1886, 103, 629.

[11] See Oxide and Sulphide.

[12] Meyerhoffer, *Zeitsch. physikal. Chem.*, 1901, 38, 315; Parker, *Trans. Chem. Soc.*, 1918, 113, 396.

[13] Dulong, *Ann. Chim.*, 1812, [1], 82, 275 ; Rose, *Jahresber.*, 1855, 273 ; Malaguti, *Ann. Chim. Phys.*, 1857, [3], 51, 340, Guldberg and Waage, *Ostwald's Klass.*, No. 104, pp. 32 *et seq.* (Engelmann), 1899.

[14] Rose, *Pogg. Annalen*, 1848, 74, 569.

[15] Kohlrausch, *Zeitsch. physikal. Chem*, 1908, 64, 152; see also Holleman, *ibid.*, 1893, 12, 130.

[16] Melcher, *J. Amer. Chem. Soc.*, 1910, 32, 55.

heat of solution is -6.0 Cal.[1] Thomsen, from precipitation data, deduced the value -5.580 Cal.[2]

Higher values for the solubility have been obtained owing to super-saturation.[3] According to Hulett, the solubility depends on the size of the solid particles in equilibrium with the solution. By grinding so finely that the diameter of a particle is less than 0.001 mm., the solubility may reach 4.15 mgm., or 0.0355 milli-equivalents per litre at 25° C., or with barytes 6.18 mgm.[1]

The solubility is reduced by salts with a common ion, including sulphuric acid if dilute.[5] Other salts[6] and acids increase it. The effect of nitric and hydrochloric acids is shown in the following table[7] :—

C c. containing 1 milli-equivalent of Acid.	Increase in Solubility at 20° C. in mgm. $BaSO_4$ per milli-equivalent of Acid	
	HCl.	HNO_3
0.2	0.017	0.048
0.5	0.055	0.084
1	0.088	0.106
2	0.130	0.137

The solubility is increased in 40 per cent. hydrobromic and hydriodic acids,[8] and in metaphosphoric acid solutions.[9] Barium sulphate is very soluble in concentrated sulphuric acid,[10] and also to a considerable extent in hydrogen peroxide.[11] The latter fact has a bearing on the preparation of hydrogen peroxide.

Owing to its insolubility barium sulphate is used in quantitative analysis for the estimation of barium or sulphate, and the conditions necessary for satisfactory precipitation have been studied by numerous investigators. The chief sources of error are naturally the increased solubility of the precipitate due to the presence of other substances in solution, and the adsorption of foreign substances by the precipitated sulphate.[12]

Barium sulphate has the power of precipitating colloidal solutions, for example colloidal gold or arsenious sulphide. The action is mechanical.[13]

Barium sulphate alone, on account of its slight solubility, does not

[1] Melcher, J. Amer. Chem. Soc., 1910, 32, 55.

[2] Thomsen, Thermochemistry (Longmans, Green & Co.), 1908, pp. 117, 118, 323.

[3] Fresenius and Hintz, Zeitsch. anal. Chem., 1896, 35, 170 ; see Kuster, Zeitsch. anorg. Chem., 1896, 12, 261.

[4] Hulett, Zeitsch. physikal. Chem., 1901, 37, 396 ; 1904, 47, 357.

[5] Karaoglanow, Zeitsch. anal. Chem., 1917, 56, 225.

[6] Fraps, Amer. Chem. J., 1902, 27, 288 ; Erdmann, J. prakt. Chem., 1858, [1], 75, 214 ; Gutkowsky, Ber., 1872, 5, 330 ; Karaoglanow, loc. cit.

[7] Ostwald and Banthisch, J. prakt. Chem., 1884, [2], 29, 52.

[8] Haslam, Chem. News, 1886, 53, 87.

[9] Erdmann, loc. cit. ; Scheerer, J. prakt. Chem., 1858, [1], 75, 113.

[10] See Acid Sulphates.

[11] Gawalowski, Chem. Zentr., 1906, ii, 7.

[12] See Quantitative Estimation of Barium.

[13] Vanino, Ber., 1902, 35, 662 ; Vanino and Hartl, ibid., 1904, 37, 3620.

go through the same setting and hardening process as calcium sulphate, but hardening may be effected by mixing finely divided barytes with a 10 per cent. solution of aluminium, iron, or magnesium chloride, which acts by increasing the solubility.[1]

According to Tingle [2] there are three hydrates of barium sulphate : $10BaSO_4.H_2O$, separating from a hot neutral solution ; $10BaSO_4.2H_2O$, from a hot acid solution ; and $10BaSO_4.4H_2O$, from a cold acid solution.

Barium sulphate is used in the production of permanent white and lithopone, and also for glazing and weighting paper.

Several double salts are known, for example $BaSO_4.SbSO_4.6H_2O$,[3] $2BaSO_4.3TiSO_4$,[4] and $BaSO_4.Sn(SO_4)_2.3H_2O$.[5] The freezing-point curve of mixtures of barium and sodium sulphates apparently indicates the existence of the compound $BaSO_4.6Na_2SO_4$, but it has not been isolated, and, from the form of the curve, it is very easily dissociated.[6]

Acid Barium Sulphates.—Barium sulphate dissolves in hot concentrated sulphuric acid, forming a golden-yellow solution which deposits doubly refracting, needle-like crystals of $BaH_2(SO_4)$, on cooling.[7] It is readily decomposed by excess of water, but in presence of a small quantity of water it forms $BaH_2(SO_4)_2.2H_2O$, which sets to a hard mass if kept in a desiccator.[8] The same hydrate is obtained in crystalline needles by exposing the solution to the air.[9] A second hydrate, $BaH_2(SO_4)_2.H_2O$, has also been isolated.[10] The anhydrous compound is decomposed at about 160° C., giving barium sulphate.

When examining the solubility of barium sulphate in sulphuric acid at low temperatures, Kendall and Davidson isolated the compound $BaSO_4.3H_2SO_4$.[11]

Solid phase, sulphuric acid :—

Temperature, °C.	10·4	9·1	6·6	2·8	−3·2	−6·6	−7·3
Molecules per cent.							
$BaSO_4$	0	0·95	2·12	3·50	5·46	6·50	6·70

Solid phase, $BaSO_4.3H_2SO_4$:—

Temperature, °C.	5·7	9·3	12·4	10·0	21·5	23·0
Molecules per cent.						
$BaSO_4$	6·70	7·05	7·30	8·09	8·28	8·59

Solutions containing 8–8·6 molecular percentage of barium sulphate deposited, on long standing, crystals which did not redissolve at 25° C., and which may have been $BaH_2(SO_4)_2$. The compound $BaSO_4.3H_2SO_4$ must, therefore, be considered as a metastable phase in this region.

By passing an electric current through a solution of barium sulphate in sulphuric acid it is found that barium migrates to the anode, indicating

[1] Rohland, *Zeitsch. anorg Chem.*, 1904, **38**, 311.
[2] Tingle, *J. Soc. Chem. Ind.*, 1918, **37**, 275R.
[3] Kühl, *Zeitsch. anorg. Chem.*, 1907, **54**, 256.
[4] Weinland and Kühl, *ibid.*, 1907, **54**, 253.
[5] Weinland and Kühl, *Ber.*, 1906, **39**, 2951.
[6] Calcagni, *Atti R. Accad. Lincei*, 1912, [4], **21**, i, 483.
[7] Rohland, *Zeitsch. anorg. Chem.*, 1910, **66**, 206 ; see also Garside, *Chem. News*, 1875, **31**, 245 ; Schultz, *Pogg. Annalen*, 1868, **133**, 137 ; Berzelius, *Annalen*, 1843, **46**, 250.
[8] Rohland, *loc. cit.*
[9] Schultz, *loc. cit.* ; Berzelius, *loc. cit.*
[10] Volchonsky, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1180.
[11] Kendall and Davidson, *J. Amer. Chem. Soc.*, 1921, **43**, 979.

that barium hydrogen sulphate is probably to be regarded as a complex acid of the formula $H_2[Ba(SO_4)_2]$.[1]

The existence of a complex acid, $H_2Ba_5(SO_4)_6$, forming barium, strontium, calcium, and potassium salts also appears to be possible.[2]

Barium Pyrosulphate, BaS_2O_7, may be formed by the action of fuming sulphuric acid on barium sulphate at 150° C.,[3] by the action of excess of chlorosulphonic acid on barium sulphate,

$$BaSO_4 + SO_3HCl = BaS_2O_7 + HCl,[1]$$
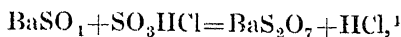
or by heating together sulphur trioxide and barium sulphate in a closed tube.[4]

Barium pyrosulphate absorbs moisture on exposure to air and reacts vigorously with water.[1] It does not melt when heated, but decomposes at a low red heat.[3]

Barium Persulphate, BaS_2O_8, may be obtained in solution by the action of persulphuric acid on barium hydroxide. It can be prepared by grinding solid barium hydroxide into a paste with a saturated aqueous solution of ammonium persulphate, driving off most of the ammonia by a current of air, and the rest *in vacuo* over sulphuric acid, and removing excess of baryta with carbon dioxide. On evaporating the filtrate *in vacuo*, small, transparent, non-deliquescent, monoclinic prisms of composition $BaS_2O_8.4H_2O$ are obtained.

At 0° C. 100 parts of water dissolve 52·2 parts of crystallised salt. The solubility increases rapidly with temperature, but supersaturated solutions are easily obtained. The solution gradually decomposes and precipitates barium sulphate, especially if heated. The solid salt is best preserved in a moist atmosphere, but heat at once decomposes it.

By treatment with absolute alcohol the monohydrate, $BaS_2O_8.H_2O$, is formed. It cannot be further dehydrated without decomposition. The salt has the oxidising properties of the persulphates.[5]

BARIUM AND SELENIUM.

Barium Selenide, BaSe, may be prepared by the reduction of barium selenate by hydrogen at 500° C.,[6] or by heating selenium with barium oxide or carbonate.[7] It forms a white powder which is yellow when hot. If heated too strongly it becomes red, due to the separation of free selenium. It is readily oxidised in the air, and excess of bromine water rapidly transforms it into selenate.[6]

The molecular heat of formation is 61·04 Cal.[8]

Like the other alkaline earth selenides, barium selenide may be obtained in a phosphorescent state.[9]

[1] Riesenfeld and Feld, *Zeitsch. Elektrochem.*, 1920, **26**, 286; Meyer and Friedrich, *Zeitsch. physikal. Chem.*, 1922, **101**, 498.

[2] Balareff, *Zeitsch. anorg. Chem.*, 1922, **123**, 69.

[3] Schultz-Sellack, *Ber.*, 1871, 4, 111.

[4] Schulze, *ibid.*, 1884, **17**, 2705.

[5] Marshall, *Trans. Chem. Soc.*, 1891, **59**, 779.

[6] Fabre, *Ann. Chim. Phys.*, 1887, [6], **10**, 517; Henglein and Roth, *Zeitsch. anorg. Chem.*, 1923, **126**, 227.

[7] Kittlemann, *Ann. Physik*, 1915, [4], **46**, 177.

[8] de Forcrand, *Ann. Chim. Phys.*, 1911, [8], **24**, 272; see also Fabre, *loc. cit.*

[9] Pauli, *Ann. Physik*, 1912, [4], **38**, 870; Kittlemann, *loc. cit.*; see Calcium Selenide.

Barium Selenite, BaSeO$_3$, is obtained by precipitation from solutions of barium nitrate and sodium selenite.[1]   Stable, microscopic, prismatic crystals are formed, containing 1 molecule of water, BaSeO$_3$.H$_2$O.[2]

An acid salt, BaSe$_2$O$_5$, is obtained by evaporating a solution of barium carbonate in excess of selenious acid.   It is only slightly soluble.[1]

Barium Selenate, BaSeO$_4$, is obtained by precipitating a solution of a barium salt with selenic acid or an alkali selenate, or by fusion of an alkali selenate with a mixture of sodium and barium chlorides.[3] By the latter method orthorhombic prisms, isomorphous with barium sulphate, and of density 4·75, are formed.   They are usually colourless, but may have a sky-blue tint, and the coloured crystals show pleochroism.

The precipitated salt has a density of 4·67 at 22° C.[4]   It adsorbs foreign salts in its formation even more readily than barium sulphate,[5] making it difficult to determine selenic acid by barium.   It is more soluble in water than barium sulphate, a litre of the solution saturated at 25° C. containing 82·49 mgm. of barium selenate.[6]   When strongly heated it is completely converted into barium selenite.   Reduction to selenite, accompanied by the evolution of chlorine, takes place when the salt is boiled with hydrochloric acid.

Acid Barium Selenate, BaSeO$_4$.H$_2$SO$_4$, has been obtained similarly to the acid sulphate by dissolving barium selenate in selenic acid.   By electrolytic transport it can be caused to crystallise round the anode, and so it is probably to be regarded as barium selenic acid, H$_2$[Ba(SeO$_4$)$_2$].   A concentrated solution of selenic acid saturated with barium selenate also deposits crystals of barium selenic acid.[7]

BARIUM AND TELLURIUM.

Barium Telluride.—An impure telluride is obtained by reducing barium tellurate with hydrogen above 310° C.[8]

Barium Tellurite, BaTeO$_3$, may be obtained as a voluminous white precipitate from dilute solutions of an alkali tellurite and barium chloride.   It always contains an amount of the latter which varies with the proportions used.   With excess of barium chloride the precipitate may have the composition 8BaTeO$_3$.5BaCl$_2$.4H$_2$O, and with equivalent quantities of the two salts, 20BaTeO$_3$.$\frac{1}{2}$BaCl$_2$.20H$_2$O.[9]

It may also be prepared by fusing together tellurium oxide and barium carbonate.   Carbon dioxide is driven off and a yellow liquid formed which gives a colourless crystalline mass on cooling.

By fusion at incipient red heat an acid salt may be obtained as a clear colourless glass.   The same compound is also formed as a

[1] Nilson, *Bull. Soc. chim.*, 1874, [2], **21**, 253.

[2] But see Muspratt, *J. Chem. Soc.*, 1850, **2**, 60.

[3] Michel, *Compt. rend.*, 1888, **106**, 878.

[4] Schafarik, *J. prakt. Chem.*, 1863, **90**, 12

[5] Metzner, *Ann. Chim. Phys.*, 1898, [7], **15**, 225.

[6] Meyer and Friedrich, *Zeitsch. physikal. Chem.*, 1922, **102**, 369 ; see also Pettersson, *Zeitsch. anal. Chem.*, 1873, **12**, 287.

[7] Meyer and Friedrich, *Zeitsch. physikal. Chem.*, 1922, **101**, 498.

[8] Henglein and Roth, *Zeitsch. anorg. Chem.*, 1923, **126**, 227.

[9] Lenher and Wolesensky, *J. Amer. Chem. Soc.*, 1913, **35**, 718.

voluminous flocculent precipitate by the action of very dilute nitric acid on the neutral salt.[1]

Barium Tellurate, $BaTeO_4$, is formed as a voluminous precipitate by mixing solutions of barium chloride and a neutral tellurate. It is only slightly soluble in cold water, but is much more soluble in hot, and very soluble in nitric acid. It contains 3 molecules of water which it loses above 200° C.[1] The density of the hydrated salt is 4·48 at 16° C., and of the anhydrous salt 4·2.[2]

An acid salt, $BaH_2Te_2O_8$, which is more soluble than the neutral salt and is decomposed by water, is also known, as well as a salt containing four equivalents of acid to one of barium.[1]

BARIUM AND CHROMIUM.

Barium Chromite, $BaCr_2O_4$, is obtained as a dense green crystalline powder by heating a mixture of potassium dichromate and barium chloride to redness.[3] By heating together chromium sesquioxide and barium oxide in the electric furnace a polychromite, $BaO.4Cr_2O_3$, is produced, even when excess of baryta is present. It forms a greenish-brown powder of density 5·4 at 15° C.[4]

Barium Chromate, $BaCrO_4$, is obtained as a pale yellow powder of density 4·3–4·5[5] by precipitation from solutions of a chromate and a soluble barium salt.[6] It can be prepared in the form of rhombic crystals, isomorphous with barium sulphate and of density 4·6, by fusing sodium and potassium chromates with barium chloride.[7]

Barium chromate is stable at red heat, and for that reason has been employed in painting porcelain. It is practically insoluble in acetic acid, but is readily dissolved by hydrochloric, nitric, and chromic acids. It is decomposed by sulphuric acid and by a hot solution of sodium carbonate. In the latter case a definite equilibrium point, between barium chromate and sodium carbonate on the one hand, and barium carbonate and sodium chromate on the other, is reached.[8]

The solubility has been determined by electrical conductivity methods.[9]

Temperature, °C.	−0·88	16·07	17·42	18	28·08
Mgm. $BaCrO_4$ per litre	2·04	3·37	3·48	3·52	4·36
Milli-equiv. per litre	0·0161	0·0266	0·0275	0·0278	0·0344

Barium chromate is soluble in molten sodium nitrate.[10]

By precipitation from concentrated solutions a barium potassium

[1] Berzelius, *Ann. Chim. Phys.*, 1835, [2], 58, 257.
[2] Clarke, *Jahresber.*, 1877, 43.
[3] Gerber, *Bull. Soc. chim.*, 1877, [2], 27, 435.
[4] Dufau, *Ann. Chim. Phys.*, 1897, [7], 12, 257.
[5] Schafarik, *J. prakt. Chem.*, 1863, 90, 1 ; Schröder, *Annalen*, 1874, 172, 278,
[6] Morris, *Annalen*, 1882, 213, 253 ; Khroustschoff and Martinoff, *Ann. Chim. Phys.* 1887, [6], 11, 234.
[7] Bourgeois, *Compt. rend.*, 1879, 88, 382.
[8] Rose, *Pogg. Annalen*, 1855, 95, 426 ; Malaguti, *Ann. Chim. Phys.*, 1857, [3], 51, 336.
[9] Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, 64, 157 ; see also Meschezerski, *Zeitsch. anal. Chem.*, 1882, 21, 399 ; Fresenius, *ibid.*, 1890, 29, 413 ; Waddell, *Analyst*, 1918, 43, 287, who all obtain higher values.
[10] Guthrie, *Trans. Chem. Soc.*, 1885, 47, 94.

chromate, $BaCrO_4.K_2CrO_4$,[1] and a barium ammonium chromate, $BaCrO_4.(NH_4)_2CrO_4$,[2] may be obtained.

Barium Dichromate, $BaCr_2O_7$, is obtained by heating together solid chromic acid and moist, freshly precipitated barium chromate mixed with potassium chromate and potassium dichromate,[3] or by boiling freshly precipitated barium chromate with chromic acid and nitric acid,[4] or, finally, by decomposing the chromate with dilute sulphuric acid.[5] It crystallises in slender, yellowish-brown, rhombic prisms as $BaCr_2O_7.2H_2O$, the 2 molecules of water being lost at about 100° C.[6] Barium dichromate is decomposed by water, giving the chromate.

Barium Potassium Trichromate, $2BaCr_3O_{10}.K_2Cr_3O_{10}.H_2O$, has been obtained as a very hygroscopic compound readily decomposed by water.[5]

Barium Chlorochromate, $Ba(CrO_3Cl)_2.4CH_3COOH.2H_2O$, has been obtained by the action of chromyl chloride on barium chromate in the presence of acetic acid.[7] It is an unstable compound crystallising in yellow plates. In dry air it gives up acetic acid and chromyl chloride, and it is also decomposed by water. By treating the mother liquors from the above preparation with hydrochloric acid a compound, $BaCl(CrO_3Cl)$, is obtained, and if the acid is dilute the compound contains 2 molecules of water and forms golden-yellow, hygroscopic needles.

Barium Perchromate, $BaCrO_5$.—By treating chromic acid with an excess of hydrogen peroxide and decomposing the liquid obtained by cooled barium hydroxide solution, a very unstable, pale yellow-coloured precipitate of the perchromate is obtained. It may be washed by decantation and dried over sulphuric acid *in vacuo*. It is detonated by heat or shock. With dilute sulphuric acid it turns blue and gives up oxygen.[8]

BARIUM AND MOLYBDENUM.

Barium Molybdate, $BaMoO_4$, is obtained as a fine white crystalline powder by precipitating barium chloride with neutral sodium molybdate,[9] or with an ammoniacal solution of ammonium molybdate.[10] It may be obtained in long needles by heating sodium molybdate with a mixture of sodium and barium chlorides.[11] The density is 4·659 at 17·5° C.[12] The solubility in water is not very great, one part dissolving in 17,200 parts of water at 23° C., but it is increased by ammonium nitrate, and the salt is readily soluble in acids.[9]

A number of acid salts of varying degrees of complexity, containing up to nine equivalents of molybdic acid for each equivalent of barium,

[1] Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185; Barre, *Compt. rend.*, 1914, 158, 495.
[2] Gröger, *Zeitsch. anorg. Chem.*, 1908, 58, 412.
[3] Autenrieth, *Ber.*, 1902, 35, 2062.
[4] Mayer, *ibid.*, 1903, 36, 1742; see also Zettnow, *Pogg. Annalen*, 1872, 145, 167; Bahr, *J. prakt. Chem.*, 1853, [1], 60, 60.
[5] Bahr, *loc. cit.*
[6] Preis and Rayman, *Ber.*, 1880, 13, 340.
[7] Pratorius, *Annalen*, 1880, 201, 19.
[8] Péchard, *Compt. rend.*, 1891, 113, 39.
[9] Smith and Bradbury, *Ber.*, 1891, 24, 2930.
[10] Svanberg and Struve, *Annalen*, 1848, 68, 298; *J. prakt. Chem.*, 1848, [1], 44, 257.
[11] Schultze, *Annalen*, 1863, 126, 49.
[12] Clarke and Marsh, *Amer. J. Sci.*, 1877, [3], 14, 281.

have been obtained.[1] There are also various complex salts—with iodic [2] and periodic [3] acids, with metaphosphoric and arsenious acids,[4] with arsenic acid,[5] and with oxalic acid.[6]   A barium thiomolybdate has been mentioned.[7]

Barium Permolybdate, $Ba(MoO_4)_2.2H_2O$, is precipitated in the form of yellow, microscopic, octahedral crystals by the action of ammonium permolybdate on barium chloride, or of hydrogen peroxide on barium dimolybdate at 80° C.[8]   No precipitate is obtained in the cold. When heated the crystals become white, and water and oxygen are given off leaving a residue of barium dimolybdate.

A complex compound with oxalic acid has been described.[9]

BARIUM AND TUNGSTEN.

Barium Tungstate, $BaWO_4$, is obtained as a heavy white precipitate from hot solutions of sodium tungstate and barium chloride.   This method has been suggested for the estimation of tungsten.[10]   The salt can also be prepared by fusing sodium tungstate with barium and sodium chlorides,[11] when it forms quadratic octahedra [12] of density 6·35 at 20° C.[13]   The precipitated salt is hydrated, the amount of water present depending on the method of preparation.   A gelatinous compound with 4 molecules of water has been obtained, and a crystalline one with 2 molecules,[14] and still other variations have been mentioned.

Barium tungstate is more soluble in ammonium nitrate solutions than in pure water, and is decomposed by acids with the separation of yellow tungstic acid.[15]   Its employment in painting has been suggested.[16]

Numerous acid tungstates have been described,[17] including paratungstates and metatungstates.

[1] Svanberg and Struve, *loc. cit.* ; Ullik, *Annalen*, 1867, **144**, 336 ; Bailhache, *Compt. rend.*, 1901, **133**, 1212 ; Junius, *Zeitsch. anorg. Chem.*, 1905, **46**, 433 ; Wempe, *ibid.*, 1912, **78**, 320 ; Rosenheim and Felix, *ibid.*, 1913, **79**, 292 ; Mawrow and Nikolaw, *ibid.*. 1915, **92**, 141.

[2] Chrétien, *Compt. rend.*, 1896, **123**, 178.

[3] Blomstrand, *Zeitsch. anorg. Chem.*, 1892, **1**, 10.

[4] Gibbs, *Jahresber.*, 1885, 527.

[5] Weinland and Sommer, *Zeitsch. anorg. Chem.*, 1897, **15**, 42 ; Pufahl, *Ber.*, 1884, **17**, 217

[6] Péchard, *Compt. rend.*, 1889, **108**, 1052 ; Itzig, *Zeitsch. anorg. Chem.*, 1899, **21**, 16.

[7] Berzelius, *Pogg. Annalen*, 1826, **7**, 261.

[8] Péchard, *Compt. rend.*, 1892, **114**, 1358 ; *Ann. Chim. Phys.*, 1893, [6], **28**, 557 ; see also Barwald, *Chem. Zentr.*, 1885, 424.

[9] Mazzucchelli, *Atti R. Accad Lincei*, 1907, [5], **16**, i, 963.

[10] Smith and Bradbury, *loc. cit.* ; see also Zettnow. *Pogg. Annalen*, 1867, **130**, 16, 240 ; Scheibler, *J. prakt Chem.*, 1861, [1], **83**, 273 ; Lefort, *Ann. Chim. Phys.*, 1878, [5], **15**, 321 ; Anthon, *J. prakt. Chem.*, 1836, [1], **9**, 337.

[11] Geuther and Forsberg, *Annalen*, 1861, **120**, 272.

[12] Michel, *Bull. Soc. franç. Min* , 1879, **2**, 142.

[13] Zambonini, *Zeitsch. Kryst. Min.*, 1905, **41**, 61.

[14] Péchard, *Compt. rend.*, 1889, **108**, 1167 ; *Ann. Chim. Phys.*, 1891, [6], **22**, 202.

[15] Smith and Bradbury, *loc. cit.*

[16] Sacc, *Compt. rend.*, 1869, **68**, 310.

[17] Lefort, *loc. cit.* ; *Ann. Chim. Phys.*, 1879, [5], **17**, 476 ; Scheibler, *J. prakt. Chem.*, 1860, [1], **80**, 204 ; 1861, [1], **83**, 273 ; Lotz, *Annalen*, 1854, **91**, 60 ; *Ann. Chim. Phys.*, 1855, [3], **43**, 246 ; von Knorre, *Ber.*, 1885, **18**, 326 ; Zettnow. *loc. cit.* ; Wyrouboff, *Bull. Soc. franç. Min.*, 1892, **15**, 63 ; Copaux, *Ann. Chim. Phys.*, 1909, [8], **17**, 217 ; *Zeitsch. anorg. Chem.*, 1912, **74**, 351.

A number of complex compounds, thio-, phospho-, arseno-, boro-, silico-, and vanadio-tungstates are known, and also a number of double salts with the alkalies and ammonia.[1]

A barium tungsten bronze, $BaO.WO_2.4WO_3$, has been prepared by reducing barium paratungstate with hydrogen at red heat,[2] and there are also barium alkali compounds similar to the calcium and strontium alkali bronzes.[3]

BARIUM AND URANIUM.

Barium Uranate, $BaUO_4$, may be obtained by fusing green oxide of uranium with barium chloride. It forms brilliant yellow crystals, insoluble in water, but readily soluble in dilute hydrochloric acid.[4]

Barium Diuranate, BaU_2O_7, may be obtained by calcining the double barium uranyl acetate or precipitating it with barium hydroxide,[5] or by heating green uranium oxide with barium chlorate.[4] By crystallisation from solution in fused barium or sodium chloride it is obtained in yellowish-green leaflets.

A hydrated uranate is obtained as a yellow precipitate by the addition of ammonia to a mixture of barium chloride and uranyl nitrate solutions, or by precipitating uranyl nitrate with excess of barium hydroxide solution.

Barium Peruranate.—By precipitating sodium peruranate with barium chloride, an orange-coloured crystalline powder of composition $(BaO_2)_2UO_4.8H_2O$ is obtained.[6] If ammonium peruranate be used instead of the sodium compound, a yellow flocculent precipitate, $BaO_2(UO_4)_2.9H_2O$, is formed. Both are decomposed by carbon dioxide, forming hydrogen peroxide, barium carbonate, and uranium tetroxide.[7]

BARIUM AND NITROGEN.

Barium Nitride, Ba_3N_2.—As in the case of the other alkaline earths, an impure barium nitride was first obtained by heating barium amalgam in a current of nitrogen when the mercury distils off, leaving, in general, a fused compact mass with a crystalline fracture, but sometimes yellowish needles.[8] Metallic barium absorbs nitrogen at 260°–600° C. to form the nitride.[9] It may also be formed as a voluminous yellow powder, along with ammonia, by heating the amide, $Ba(NH_2)_2$, to above 650° C.,[10] or *in vacuo* at 400°–450° C.[11] The reaction is reversible.

Barium nitride is an orange-yellow solid, fusible above 1000° C. and slightly volatile. With water, barium hydroxide and ammonia are

[1] Copaux, *loc. cit.* ; Gibbs, *Jahresber.*, 1885, 527 ; Péchard, *Ann. Chim. Phys.*, 1891, [6], **22**, 194 ; Klein, *ibid.*, 1883, [5], **28**, 350 ; see also Moissan, *Traité de Chimie Minérale* (Masson et Cie), 1905, vol. iv.

[2] Hallopeau, *Thèse*, Paris, 1899, No. 1006, p. 32.

[3] Engels, *Zeitsch. anorg. Chem.*, 1903, **37**, 125.

[4] Ditte, *Compt. rend.*, 1882, **95**, 988.

[5] Wertheim, *Ann. Chim. Phys.*, 1844, [3], **11**, 59

[6] Melikoff and Pissarjewsky, *Ber.*, 1897, **30**, 2902.

[7] Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.*, 1898, **18**, 59.

[8] Maquenne, *Compt. rend.*, 1892, **114**, 25, 220 ; *Bull. Soc. chim.*, 1892, [3], **7**, 366 ; *Ann. Chim. Phys.*, 1893, [6], **29**, 219 ; see also Wolk, *Bull. Soc. chim.*, 1910, [4], **7**, 830.

[9] Dafert and Miklauz, *Monatsh.*, 1913, **34**, 1685.

[10] Mentrel, *Compt. rend.*, 1902, **135**, 740.

[11] Guntz and Mentrel, *Bull. Soc. chim.*, 1903, [3], **29**, 578.

formed. At red heat it reacts energetically with carbon monoxide, giving barium hydroxide and cyanide. Maquenne suggests that nitride formation precedes that of the cyanide in the production of the latter.[1]

When hydrogen is passed over the nitride at 300° C. the hydride is formed and nitrogen liberated, ammonia being also evolved, especially if the temperature be raised. As the hydride may again be converted into the nitride by heating in nitrogen, these reactions might form the basis of a method for the synthesis of ammonia.[2]

The molecular heat of formation is 149·4 Cal.[3]

Barium Azide, Ba(N₃)₂, may be prepared by the action of hydrazoic acid on barium hydroxide, or of a boiling solution of ammonium azide on the freshly precipitated hydroxide.[4] There is, apparently, always too little barium present in the salt prepared by the second method.[5] It forms triclinic crystals containing 1 molecule of water,[6] which is removed by drying over sulphuric acid.[7]

Barium azide is not hygroscopic, and it is less soluble in water than the corresponding calcium and strontium salts, 100 parts of water dissolving 12·5 parts of the salt at 0° C. and 17·3 parts at 17° C. Only 0·0172 part dissolves in 100 parts of alcohol at 16° C. The aqueous solution is very stable and does not lose hydrazoic acid when heated.[8]

The dry salt is exploded by heat but not by shock, depositing a black powder of finely divided barium. The explosion temperature is 225° C.[9] When the salt is carefully heated *in vacuo* evolution of nitrogen begins at 160° C., and will then continue at 120° C.[10]

Barium Ammonium, Barium Hexammoniate, Ba(NH₃)₆, is obtained as a red, bronze-like solid by passing ammonia over metallic barium below 28° C. At −23° C. a blue solution of the compound in liquid ammonia is formed, and at −50° C. a second liquid phase separates.[11] Below −15° C. barium ammonium is stable. At higher temperatures it decomposes to form the amide.[11] The following values have been found for the dissociation pressure of ammonia at different temperatures : 13 mm. at −25° C., 50 mm. at −3° C., and 60 mm. at 0° C.[12] The heat of formation of barium hexammoniate from barium and ammonia is 9·68 Cal.[12] Barium ammonium inflames spontaneously in the air and reacts violently with water. It absorbs oxygen giving a mixture of barium peroxide and oxide. With nitric oxide it forms barium hyponitrite, and with carbon monoxide, barium carbonyl.[11]

Barium ammonium may also be obtained by dissolving a 60 per cent. barium amalgam in liquid ammonia.[13]

[1] Maquenne, *loc. cit.*

[2] Dafert and Miklauz, *Monatsh.*, 1913, **34**, 1685.

[3] Guntz and Mentrel, *Bull. Soc. chim.*, 1903, [3], **29**, 578.

[4] Curtius, *Ber.*, 1890, **23**, 3032; Curtius and Rissom, *J. prakt Chem.*, 1898, [2], **58**, 287; Dennis and Benedict, *Zeitsch. anorg. Chem.*, 1898, **17**, 22; *J. Amer. Chem. Soc.*, 1898, **20**, 225; Dennis and Browne, *ibid.*, 1904, **26**, 602; *Zeitsch. anorg. Chem.*, 1904, **40**, 97.

[5] Curtius and Rissom, *loc. cit.*

[6] Dennis and Benedict, *loc. cit.*

[7] Dennis and Browne, *loc. cit.*

[8] Curtius and Rissom, *loc. cit.*; but see Dennis and Benedict, *loc. cit.*

[9] Hitch, *J. Amer. Chem. Soc.*, 1918, **40**, 1203. 152° C. has also been given as the explosion temperature, Wöhler and Martin, *Zeitsch. angew. Chem.*, 1917, **30**, 33.

[10] Tiede, *Ber.*, 1916, **49**, 1742.

[11] Mentrel, *Compt. rend.*, 1902, **135**, 740.

[12] Biltz and Hüttig, *Zeitsch. anorg. Chem.*, 1920, **114**, 241; Biltz, *Zeitsch. Elektrochem.*, 1920, **26**, 374.

[13] Guntz and Mentrel, *Bull. Soc. chim.*, 1903, [3], **29**, 585.

Barium Amide, Ba(NH$_2$)$_2$.—If barium be heated in a current of dry ammonia at 200° C., barium amide, or baramide, Ba(NH$_2$)$_2$, is obtained as a greyish-white mass. It darkens and liquefies at 280° C., and becomes green at 340° C. At higher temperatures, 460° C. in dry ammonia, or 430° C. *in vacuo*, it decomposes with formation of the nitride which, when heated in ammonia at 400° C., is partially reconverted into the amide.[1]

If the compound of barium bromide with ammonia, BaBr$_2$.8NH$_3$, is left in contact with potassium ammonium for two or three days, hydrogen is evolved and barium amide and potassium bromide are left. The latter is removed by liquid ammonia.[2]

$$BaBr_2 + 2NH_3K = Ba(NH_2)_2 + 2KBr + H_2.$$
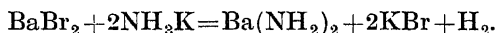
Barium amide is also formed as a white precipitate by the action of potassamide on an excess of a barium salt in liquid ammonia solution.[3]

An amide of the composition Ba$_3$(NH$_2$)$_2$ has been obtained by the absorption of hydrogen by barium nitride. It is less stable than the corresponding calcium and strontium compounds, and reacts readily with a further quantity of hydrogen at low temperatures to give the hydride and nitrogen, a certain amount of ammonia being also evolved.[4]

By pouring a solution of a barium salt in liquid ammonia into excess of a solution of potassamide, a microcrystalline precipitate of potassium ammonobarate, BaNK.2NH$_3$, or Ba(NH$_2$)$_2$.KNH$_2$, is formed, similar to potassium ammonocalciate and strontianate.[3] It is unchanged by heating to 100° C. It is insoluble in liquid ammonia, but is decomposed and dissolved in liquid ammonia solutions of ammonium nitrate. Water readily hydrolyses it into potassium and barium hydroxides and ammonia.

Barium Amidosulphonate, Ba(H$_2$NSO$_3$)$_2$, is obtained by the action of the sodium salt on a concentrated solution of barium chloride.[5] A dibarium oxyamidosulphonate, Ba$_2$(SO$_3$NOH)$_2$.H$_2$O,[6] and a monobarium compound, Ba(SO$_3$NHOH)$_2$.H$_2$O,[7] have also been isolated.

Barium Imide.—Imide formation by heating metallic barium, barium nitride, or the hydride in a mixture of hydrogen and nitrogen is doubtful.[4]

Barium Imidosulphonate, Ba$_3$N$_2$(SO$_3$)$_4$.5H$_2$O, has been prepared, and also an acid salt and several double salts with mercury and the alkalies. They decompose explosively on being heated.[8]

Barium Hyponitrite, BaN$_2$O$_2$, may be obtained as a crystalline precipitate by the action of sodium hyponitrite on barium chloride

[1] Mentrel, *Compt. rend.*, 1902, **135**, 740 ; Guntz and Mentrel, *Bull. Soc. chim.*, 1903, [3], **29**, 578.

[2] Joannis, *Compt. rend.*, 1905, **140**, 1243.

[3] Franklin, *J. Amer. Chem. Soc.*, 1915, **37**, 2295.

[4] Dafert and Miklauz, *Monatsh.*, 1913, **34**, 1685.

[5] Divers and Haga, *Trans. Chem. Soc.*, 1896, **69**, 1653 ; *Chem. News*, 1896, **74**, 277 ; Berglund, *Ber.*, 1876, **9**, 1896.

[6] Frémy, *Ann. Chim. Phys.*, 1845, [3], **15**, 408 ; Divers and Haga, *Trans. Chem. Soc.*, 1889, **55**, 760.

[7] Divers and Haga, *loc. cit.*

[8] Divers and Haga, *Trans. Chem. Soc.*, 1892, **61**, 964 ; 1896, **69**, 1622 ; *Chem. News*, 1896, **74**, 269 ; Berglund, *Ber.*, 1876, **9**, 252 ; *Jahresber.*, 1876, 177 ; Jacquelain, *Ann. Chim. Phys.*, 1843, [3], **8**, 293.

solution,[1] or of the silver salt on an ammoniacal solution of barium acetate and subsequent washing of the precipitate with ammonia, alcohol, and ether, followed by rapid drying in air.[2] Large needles are obtained when very dilute solutions are used. It is also produced by the action of nitric oxide on barium ammonium.[3]

It is obtained both as the anhydrous salt and as the tetrahydrate, $BaN_2O_2.4H_2O$.[1] The tetrahydrate readily effloresces.[2] Barium hyponitrite is only slightly soluble in water, the solution giving an alkaline reaction. It is decomposed by dilute acids with the evolution of nitrous acid.

An acid salt, $BaH_2(N_2O_2)_2$, crystallising in long needles and readily soluble in water, may also be prepared, but not in a pure condition.[5]

By crystallising the neutral salt from acetic acid solution a compound, $BaN_2O_2.Ba(CH_3COO)_2.2CH_3COOH.3H_2O$, is obtained. It is less stable than the corresponding calcium and strontium compounds.[6]

Barium Nitrososulphate, or Nitroxysulphite, $BaSO_3(NO)_2$, is obtained as a white precipitate by the action of barium hydroxide on the potassium salt,[7] and a double potassium barium salt has also been separated.[8]

Barium Nitrohydroxylaminate, BaN_2O_3, is obtained, by the action of the sodium salt on a barium chloride solution,[9] as a white precipitate containing 1 molecule of water of crystallisation, which it loses at 115° C.[10]

Barium Nitrite, $Ba(NO_2)_2$, is best obtained by the decomposition of silver nitrite by barium chloride.[11] It is also formed in other ways, for example by the action of nitrous acid vapours on barium hydroxide solution or barium carbonate,[12] by careful calcination of the nitrate and removal of barium oxide and nitrate,[13] or by a combination of these two methods;[14] by reduction in the dry state by copper, cuprous oxide, oxalates, or other reducing agents;[15] by the action of sodium nitrite on barium chloride in a limited amount of water;[16] and by the electrolytic reduction of barium nitrate solution.[17]

[1] Menke, *Trans. Chem. Soc.*, 1878, 33, 404; Zorn, *Ber.*, 1882, 15, 1007; Divers, *Trans. Chem. Soc.*, 1899, 75, 117.

[2] Kirschner, *Zeitsch. anorg. Chem.*, 1898, 16, 426; but see Maquenne, *Ann. Chim. Phys.*, 1889, [6], 18, 564.

[3] Mentrel, *Compt. rend.*, 1902, 135, 740; Guntz and Mentrel, *Bull. Soc. chim.*, 1903, [3], 29, 585.

[4] Divers, *loc. cit.*

[5] Zorn, *loc. cit.*

[6] Maquenne, *Ann. Chim. Phys.*, 1889, [6], 18, 569; *Compt. rend.*, 1889, 108, 1303.

[7] Divers and Haga, *Trans. Chem. Soc.*, 1885, 47, 364.

[8] Hantzsch, *Ber.*, 1894, 27, 3271.

[9] Angeli, *Chem. Zeit.*, 1896, 20, 176; *Gazzetta*, 1896, 26, ii, 17; *Atti R. Accad. Lincei*, 1896, [5], 5, i, 120.

[10] Angelico and Fanara, *Gazzetta*, 1901, 31, ii, 15.

[11] Rammelsberg, *Pogg. Annalen*, 1863, 118, 287; Arndt, *Zeitsch. anorg. Chem.*, 1901, 27, 341; Rây, *Trans. Chem. Soc.*, 1905, 87, 177; Vogel, *Zeitsch. anorg. Chem.*, 1903, 35, 385; Oswald, *Ann. Chim.*, 1914, [9], 1, 32.

[12] Fritzsche, *Pogg. Annalen*, 1840, 49, 134; Hampe, *Annalen*, 1863, 125, 337; Oswald, *loc. cit.*

[13] Hess, *Pogg. Annalen*, 1828, 12, 257; Fischer, *ibid.*, 1848, 74, 115; Hampe, *loc. cit.*; Oswald, *loc. cit.*; Rây, *loc. cit.*

[14] Hampe, *loc. cit.*

[15] Oswald, *loc. cit.*

[16] Matuschek, *Chem. Zeit.*, 1902, 26, 526; *Ber.*, 1907, 40, 990; Witt and Ludwig, *ibid.*, 1903, 36, 4384; see also Meyerhoffer, *ibid.*, 1904, 37, 261.

[17] Wenger and Lubomirski, *Ann. Chim. anal. appl.*, 1919, [2], 1, 339.

The properties of barium nitrite have been carefully examined by Oswald, and also by Râ*y. The anhydrous salt has a density of 3·52 at 0° C., melts at 217° C.,[1] and decomposes at 235° C. From solution it crystallises as the monohydrate in glistening, faintly yellow needles, isomorphous with the strontium salt and of density 3·109. This hydrate is stable in air, melts at 184° C. with partial hydrolysis, and may be dehydrated *in vacuo* over phosphorus pentoxide. It is difficult to remove all the water of crystallisation. The powdered salt dried in the steam-oven has a composition of approximately $Ba(NO_2)_2.\frac{1}{2}H_2O$. Fock obtained the anhydrous salt in hexagonal crystals by slow evaporation.[2]

The following values have been obtained for the solubility of the monohydrate at different temperatures [3]:—

Temperature, °C.	0	10	20	30	40	50	60	70	80	90	100	110
Grams $Ba(NO_2)_2.H_2O$ in 100 grams water	63 5	69·5	79 5	93	113	136	170	202	254	461	461	765

The cryohydric temperature is −6·5° C., and the cryohydrate contains 34·5 per cent. of the nitrite.

The solubility of barium nitrite is diminished by alcohol, and in 90 per cent. alcohol the salt is practically insoluble.[4] The aqueous solution has an alkaline reaction. It is stable unless acidified, when it is readily oxidised. Concentrated aqueous solutions undergo hydrolysis at 100° C.

Several double salts are known: $Ba(NO_2)_2.2AgNO_2.H_2O$,[3] $2Ba(NO_2)_2.3Hg(NO_2)_2.5H_2O$, containing the complex bivalent anion $Hg(NO_2)_4^{--}$,[5] $Ba(NO_2)_2.2KNO_2$,[2] $Ba(NO_2)_2.2KNO_2.H_2O$,[6] $2Ba(NO_2)_2.CsNO_2$, $Ba(NO_2)_2.2CsNO_2.H_2O$, $Ba(NO_2)_2.AgNO_2.3CsNO_2.2H_2O$,[7] and $Ba[Cu(NO_2)_2OH]_2$.[8]

Barium Nitrate, $Ba(NO_3)_2$, has been found in the natural state in the Chili saltpetre beds.[9] It may be obtained by neutralising nitric acid with barium hydroxide or carbonate. Owing to its slight solubility as compared with the other alkaline earth nitrates, it is precipitated in the cold by the action of sodium nitrate solution on a concentrated solution of barium chloride,[10] or of sodium nitrate on barium sulphide.[11] It may also be obtained by fusing barium sulphate with excess of calcium nitrate.[12]

The salt, as ordinarily obtained, is anhydrous. It crystallises in colourless cubical octahedra and is isomorphous with the chlorate and

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[1] See also Arndt, *loc. cit.*
[2] Fock, *Zeitsch. Kryst. Min.*, 1890, 17, 181.
[3] Oswald, *loc. cit.*
[4] Vogel, *loc. cit.*
[5] Rây, *Trans. Chem. Soc*, 1910, 97, 326.
[6] Lang, *Pogg. Annalen*, 1863, 118, 293.
[7] Jamieson, *Amer. Chem. J.*, 1907, 38, 614.
[8] Kurtenacker, *Zeitsch. anorg. Chem.*, 1913, 82, 207.
[9] Groth, *Jahrb. Min.*, 1883, i, Ref., 14; *J. Chem. Soc.*, 1883, 44, Abs. ii, 431.
[10] Kühlmann, *Ann. Chim. Phys.*, 1858, [3], 54, 396; von Lippmann, *Chem. Zeit.*, 1894, 18, 67; see also Coppodoro, *Gazzetta*, 1912, 42, i, 233; *Atti R. Accad. Lincei*, 1912, [5], 21, ii, 842.
[11] Mohr, *Annalen*, 1838, 25, 290
[12] Aktien-Gesell. f chem. Ind. and Kühne, German Patent, 248524 (1911), see *J. Soc. Chem. Ind.*, 1912, 31, 984.

bromate.[1] The density is $3 \cdot 22$ [2] and melting-point $595 \cdot 5°$ C.[3] By crystallising between $0°$ C. and $12°$ C. it may be obtained as the dihydrate.[1]

When heated strongly, barium nitrate is decomposed, giving barium oxide or peroxide, oxides of nitrogen, and oxygen.[5] Hydrogen reduces it at red heat with the formation of barium hydroxide.[6]

The heat of solution of barium nitrate is $-9 \cdot 4$ Cal.[7] It is not remarkably soluble in water. The following values have been found for the composition of solutions at different temperatures [8] :—

Temperature, °C.	.0	4	2 1	6	11	18	28 5	52	73	110	134	150	171	215
Grams $Ba(NO_3)_2$ per 100 grams solution	4 3	4 9	5 6	6 4	7·7	9·7	14 9	19 4	27 4	32 5	34·9	38 3	45 8	

The solubility is diminished by the presence of barium chloride,[9] potassium nitrate,[10] and nitric acid.[11] It is increased by barium hydroxide,[12] but no basic nitrates are formed.[13] The salt is practically insoluble in alcohol and in most organic solvents.[11]

Aqueous solutions of barium nitrate have been studied from the point of view of density,[15] boiling-point,[16] freezing-point lowering in dilute solutions,[17] viscosity,[18] and electrical conductivity.[19]

With potassium and sodium nitrates, barium nitrate forms a ternary eutectic mixture at $214 \cdot 1°$ C.[20]

A double salt is formed with barium acetate, $Ba(NO_3)(CH_3COO)$. $4H_2O$,[21] and one with potassium nitrate, $Ba(NO_3)_2.2KNO_3$,[22] and $Ba(NO_3)_2.2KNO_3.H_2O$.[23]

BARIUM AND PHOSPHORUS.

Barium Phosphide, Ba_3P_2, has been obtained similarly to strontium phosphide by reducing the phosphate with lamp-black in

[1] Traube, *Zeitsch Kryst. Min* , 1894, **23**, 133.

[2] Brugelmann, *Ber.*, 1884, **17**, 2359 ; see Clarke, *Constants of Nature* (Macmillan & Co.), 1888, p. 111.

[3] Harkins and Clark, *J. Amer. Chem Soc.*, 1915, **37**, 1826 , see also Carnelley, *Trans. Chem. Soc* , 1878, **33**, 278 ; Le Chatelier, *Bull. Soc. chim* , 1887, [2], **47**, 300.

[4] Hirzel, *Zeitsch. Pharm* , 1854, 49 ; *Jahresber* , 1854, 324.

[5] Rivière, *Bull. Soc. Mulh.*, 1866, **36**, 438.

[6] Kuhlmann, *Ann. Chim. Phys* , 1847, [3], **20**, 234

[7] Thomsen, *Thermochemistry*, English edition (Longmans, Green & Co.), 1908, p. 363.

[8] Etard, *Ann. Chim. Phys.*, 1894, [7], **2**, 527 ; see also Gay-Lussac, *Ann. Chim.*, 1791, [1], **11**, 313 ; Nordenskiold, *Pogg. Annalen*, 1869, **136**, 309.

[9] Etard, *Ann. Chim. Phys.*, 1894, [7], **3**, 287.

[10] Euler, *Zeitsch. physikal. Chem.*, 1904, **49**, 303.

[11] Vitali, *Boll. Chim. Farm* , 1907, **46**, 313.

[12] Harkins, *J. Amer Chem. Soc* , 1911, **33**, 1836.

[13] Parsons and Corson, *ibid.*, 1910, **32**, 1383.

[14] d'Ans and Siegler, *Zeitsch. physikal Chem* , 1913, **82**, 37.

[15] Kremers, recorded by Gerlach, *Zeitsch. anal. Chem.*, 1888, **27**, 283, 329.

[16] Smits, *Zeitsch. physikal. Chem.*, 1902, **39**, 418 ; Gerlach, *Zeitsch. anal. Chem.*, 1887, **26**, 449

[17] Hausrath, *Ann. Physik*, 1902, [4], **9**, 544 ; de Coppet, *Ann. Chim. Phys.*, 1872, [4], **25**, 548.

[18] Wagner, *Zeitsch. physikal. Chem.*, 1890, **5**, 31 ; *Wied. Annalen*, 1883, **18**, 259.

[19] Kohlrausch and Gruneisen, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1215 ; Kahlenberg, *J. Physical Chem.*, 1901, **5**, 339 ; Noyes, *Zeitsch. physikal. Chem.*, 1901, **36**, 75.

[20] Harkins and Clark, *J. Amer. Chem. Soc.*, 1915, **37**, 1816.

[21] Lucius, *Annalen*, 1857, **103**, 113.

[22] Wallbridge, *Amer. Chem. J.*, 1903, **30**, 154 ; Foote, *ibid.*, 1904, **32**, 251 ; Findlay, Morgan, and Morris, *Trans. Chem. Soc.*, 1914, **105**, 779.

[23] Lang, *Pogg. Annalen*, 1863, **118**, 293

the electric furnace. It is a dark-coloured compound with a brilliant crystalline fracture, and of density 3·183. It is not so readily attacked by reagents as strontium phosphide. It burns in chlorine at 90° C., and in bromine vapour at 260°–300° C. Water decomposes it in the cold with the formation of barium hydroxide and evolution of phosphoretted hydrogen.[1]

An impure phosphide is also formed by the action of phosphorus vapour on barium oxide.[2]

Barium Dihydrohypophosphite, $Ba(H_2PO_2)_2$, is obtained by heating barium hydroxide[3] or barium sulphide solution[4] with phosphorus. It is also formed by the action of water on barium phosphide,[5] or by the action of phosphoretted hydrogen on barium hydroxide solution.[6] It forms flexible monoclinic needles of the monohydrate, $Ba(H_2PO_2)_2.H_2O$, which are unchanged in air at ordinary temperatures, and lose water at 100° C.[4] It is soluble to the extent of 1 part in 3·5 of cold and 3 of boiling water, but is insoluble in alcohol. Nitric acid transforms it quantitatively into the metaphosphate, and it is decomposed by potassium hydroxide solution, liberating hydrogen and forming barium and potassium phosphites. When strongly heated it forms the pyro- and meta-phosphate[7] in the molecular proportions of 6 : 1.

Barium Hydrophosphite, $2BaHPO_3.H_2O$ or $H_4Ba_2P_2O_7$,[8] is formed by precipitation of barium chloride with ammonium phosphite.[9] It loses water between 150° C. and 200° C.[10] At higher temperatures it is decomposed, giving hydrogen, phosphorus, and barium pyrophosphate.[8]

A dihydrophosphite, $BaH_2(HPO_3)_2.H_2O$,[10] $2H_2O$,[11] or $3H_2O$,[11] which loses 1 molecule of water of crystallisation on being dried, is known.[12] Other crystalline acid salts of varying composition are also obtained by evaporating solutions of the ordinary phosphite with phosphorous acid.[13]

Barium Pyrophosphite, $BaH_2P_2O_5$, is obtained by the dehydration of the acid phosphite at 120°–160° C.[14]

Barium Hypophosphate, $BaPO_3$, is formed as a white precipitate by the action of neutral sodium hypophosphate on barium chloride.[15] It is insoluble in acetic acid, but readily soluble in hydrochloric and phosphoric acids. When heated it forms the pyrophosphate.[16]

By dissolving the neutral salt in hypophosphoric acid and evaporating in the cold, or by precipitating barium chloride with acid sodium hypophosphate, acid barium hypophosphate, $BaH_2(PO_3)_2.2H_2O$, is obtained.[17]

[1] Jaboin, *Compt. rend.*, 1899, **129**, 762.
[2] Dumas, *Ann. Chim. Phys.*, 1826, [2]. **33**, 364.
[3] Rose, *Pogg. Annalen*, 1827, **9**, 364.
[4] Wurtz, *Annalen*, 1842, **43**, 323.
[5] Dulong, *Ann. Chim. Phys.*, 1816, [2], **2**, 141.
[6] Winkler, *Pogg. Annalen*, 1860, **111**, 443
[7] Rammelsberg, *Ber.*, 1872, **5**, 492.
[8] Rammelsberg, *Pogg. Annalen*, 1867, **131**, 268.
[9] Berzelius, *Ann. Chim. Phys.*, 1816, [2], **2**, 231 ; Kraut, *Annalen*, 1875, **177**, 277 ; Rose, *Pogg. Annalen*, 1827, **9**, 23.
[10] Würtz, *Ann. Chim. Phys.*, 1846, [3], **16**, 211.
[11] Amat, *ibid.*, 1891, [6], **24**, 311.
[12] Rose, *Pogg. Annalen*, 1827, **9**, 370.
[13] Rammelsberg, *Jahresber.*, 1867, 144 ; see also Würtz, *loc. cit.*
[14] Amat, *Ann. Chim. Phys.*, 1891, [6], **24**, 354.
[15] See Rammelsberg, *J. prakt. Chem.*, 1892, [2], **45**, 153.
[16] Salzer, *Annalen*, 1878, **194**, 34.
[17] Salzer, *loc. cit.* ; Joly, *Compt. rend.*, 1886, **103**, 1197.

At 140° C. it slowly loses water of crystallisation, and at higher temperatures hydrogen escapes and burns, leaving barium metaphosphate.[1] The salt may be purified by recrystallisation from very dilute boiling nitric acid.[2]

Barium Orthophosphates. — *Tribarium Orthophosphate*, Ba_3 $(PO_4)_2$, may be formed as large transparent plates belonging to the cubic system, and of density 4·1 at 16° C., by fusing barium oxide with sodium metaphosphate at red heat, with or without sodium or barium chlorides.[3] It is obtained as the monohydrate by precipitation of excess of barium chloride by trisodium phosphate,[4] or by disodium phosphate in alkaline solution.[5] In the latter case excess of barium hydroxide solution should be added to prevent the formation of a double salt.[6] When trisodium phosphate is used a colloidal precipitate is first formed without perceptible heat change. Afterwards, crystallisation takes place with the evolution of heat. This has resulted in considerable variation in the values obtained for the heat of formation.[7] It is soluble in most acids, giving the mono- or di-barium phosphates. Its use as a pigment has been suggested.[8]

A naturally occurring barium apatite, $3Ba_3(PO_4)_2.BaCl_2$, corresponding to calcium apatite, has been found, and can be prepared artificially by fusing together barium phosphate and barium chloride.[9] There are also a bromapatite, an iodapatite, and a fluorapatite.[10]

Dibarium Orthophosphate, $BaHPO_4$, is obtained by precipitating barium chloride with disodium phosphate.[11] It is also formed by the action of phosphoric acid on tribarium phosphate,[12] or of water on monobarium phosphate.[13] It forms a white crystalline powder, probably containing 1 molecule of water of crystallisation,[14] or is obtained as barium monetite in rhombic prisms, of density 4·165 and containing no water of crystallisation.[15]

It is soluble in acids, including sulphurous acid,[16] and also in solutions of ammonia salts.

Monobarium Orthophosphate, $BaH_4(PO_4)_2$, forms anhydrous triclinic crystals of density 2·8–2·9,[17] when an acid solution of barium phosphate is evaporated.[12] With hydrochloric acid the double salt, $4BaH_4(PO_4)_2.BaCl_2$, is formed.[18]

For reasons already mentioned under calcium and strontium

[1] Salzer, *Annalen*, 1878, **194**, 3
[2] Joly, *Compt. rend.*, 1885, **101**, 1148.
[3] Ouvrard, *Ann. Chim. Phys.*, 1889, [6], **16**, 294
[4] Graham, *Pogg. Annalen*, 1834, **32**, 49.
[5] Rammelsberg, *ibid.*, 1846, **68**, 384.
[6] Villiers, *Compt. rend.*, 1887, **104**, 1103.
[7] Berthelot, *ibid.*, 1886, **103**, 911; Joly, *ibid.*, 1886, **103**, 1197; 1887, **104**, 1702.
[8] Betts, *J. Soc. Chem. Ind.*, 1917, **36**, 395.
[9] Deville and Caron, *Ann. Chim. Phys.*, 1862, [3], **67**, 451.
[10] Ditte, *ibid.*, 1886, [6], **8**, 520, 529, 536; see also von Woyczynski, *Zeitsch. anorg. Chem.*, 1894, **6**, 310; Winter, *Dissertation*, Leipzig, 1913, 1; *J. Chem. Soc.*, 1914, **106**, Abs. ii, 126.
[11] Joly, *Compt. rend.*, 1884, **98**, 1274; Skey, *Chem. News*, 1870, **22**, 61.
[12] Erlenmeyer, *Jahresber.*, 1857, 145 (footnote).
[13] Joly, *loc. cit.*
[14] Skey, *loc. cit.*; Chodnew, *J. prakt. Chem.*, 1843, [1], **29**, 201.
[15] de Schulten, *Bull. Soc. franç. Min.*, 1904, **27**, 109.
[16] Gerland, *J. prakt. Chem.*, 1871, [2], **4**, 125.
[17] Schröder, *Jahresber.*, 1879, 31.
[18] Erlenmeyer, *ibid.*, 1857, 147 (footnote).

phosphates, very little confidence can be placed in the solubility determinations for the different barium phosphates.[1]

Barium Pyrophosphate, $Ba_2P_2O_7$, may be obtained in orthorhombic prisms of density 3·9 by fusing barium oxide, phosphate, or sulphate, with potassium pyro- or meta-phosphate,[2] or as a white precipitate by mixing sodium pyrophosphate and barium chloride solutions,[3] or neutralising pyrophosphoric acid with barium hydroxide solution.[4] It crystallises from solution with 2 molecules of water.[5] It is only slightly soluble in water, but is attacked by mineral acids. If heated in hydrogen, phosphoretted hydrogen and other phosphorus compounds are evolved, and barium phosphate is left.[6]

Several acid pyrophosphates have been separated,[5] all infusible at red heat.

Barium Metaphosphate, $BaPO_3$, may be obtained by dissolving barium carbonate in excess of phosphoric acid, evaporating, and heating. It forms a white powder, which is unchanged by dilute acids and by water, but is decomposed by concentrated sulphuric acid.[7]

Polymerised compounds have also been obtained, for example barium hexametaphosphate, $Ba_3P_6O_{18}$, similar to the calcium and strontium hexametaphosphates,[8] and possibly others.[9]

Double Salts. — Several double phosphates of the alkalies with barium are known : barium potassium orthophosphate, $Ba_2K_2(PO_4)_2$,[2] or with $20H_2O$,[10] and barium sodium orthophosphate, $Ba_2Na_2(PO_4)_2$. $18H_2O$ or $20H_2O$;[11] barium sodium pyrophosphate, $6Ba_2P_2O_7.Na_4P_2O_7$. $6H_2O$;[12] and also the metaphosphates, $NaBaP_3O_9.4H_2O$, $NH_4BaP_3O_9$. H_2O, and $KBaP_3O_9.H_2O$,[13] and $Na_4Ba(PO_3)_6.8H_2O$.[14] Uranium barium metaphosphate, $Ba(UO_2)(PO_3)_2$, in thin green hexagonal plates, has been isolated.[15] There is also a mineral, *uranocircite*, $BaO.2U_2O_3$. $P_2O_5.8H_2O$.[16]

Basic Barium Phosphates.—A compound, $Ba_3(PO_4)_2.Ba(OH)_2$, corresponding to calcium tetraphosphate, has been isolated,[17] and also the compounds $3BaO.2P_2O_5$[18] and $5BaO.3P_2O_5$.[19] It is possible that these are to be regarded as salts of polyphosphoric acids rather than as basic salts.

[1] Malaguti, *Ann. Chim. Phys.*, 1857, [3], **51**, 346 , Joly, *loc. cit.*
[2] Ouvrard, *loc. cit.* ; *Compt. rend.*, 1888, **106**, 1599.
[3] Schwarzenberg, *Annalen*, 1848, **65**, 143 ; Hess, *Pogg. Annalen*, 1830, **18**, 73.
[4] Hess, *Pogg. Annalen*, 1830, **18**, 73.
[5] Pahl, *Arkiv. Kem. Min. Geol.*, 1905, **2**, 1, No. 6, see *J. Chem. Soc.*, 1906, **90**, Abs. ii, 87.
[6] Struve, *J. prakt. Chem.*, 1860, [1], **79**, 348.
[7] Maddrell, *Annalen*, 1847, **61**, 61.
[8] Ludert, *Zeitsch. anorg. Chem.*, 1894, **5**, 33.
[9] Fleitmann, *Jahresber.*, 1849, 234 ; Fleitmann and Henneberg, *Annalen*, 1848, **65**, 313 ; Lindbom, *Ber.*, 1875, **8**, 122.
[10] de Schulten, *Compt. rend.*, 1883, **96**, 706.
[11] de Schulten, *loc. cit.* ; Villiers, *Compt. rend.*, 1887, **104**, 1103.
[12] Baer, *Pogg. Annalen*, 1848, **75**, 164.
[13] Lindbom, *Ber.*, 1875, **8**, 122.
[14] Fleitmann and Henneberg, *Annalen*, 1848, **65**, 314.
[15] Colani, *Ann. Chim. Phys.*, 1907, [8], **12**, 139.
[16] Winkler, *J. prakt. Chem.*, 1877, [2], **16**, 91.
[17] von Woyczynski, *Zeitsch. anorg. Chem.*, 1894, **6**, 310.
[18] Fleitmann and Henneberg, *Annalen*, 1848, **65**, 331.
[19] Schwarz, *Zeitsch. anorg. Chem.*, 1895, **9**, 264.

Barium Thiophosphites.—Barium trithiophosphite, $Ba_3(PS_3)_2$,[1] or with $8H_2O$, in white microscopic rhombic prisms, and barium oxythiophosphite, $Ba_3P_2S_5O.8H_2O$, have been isolated.[2]

Barium Thiophosphates.—Several barium phosphates in which the oxygen has been partially or wholly replaced by sulphur have been separated. Barium trithiophosphate, $Ba_3(PS_3O)_2.20H_2O$, is obtained by the action of a solution of barium sulphide on sodium tetrathiophosphate. It is stable when dry, but is decomposed by water or dilute acids with the evolution of sulphuretted hydrogen.[1] By substituting barium hydrogen sulphide for the sulphide, the compound $Ba_3(PS_2O_2)_2$. $18H_2O$,[1] or $8H_2O$,[3] is formed. By the action of excess of barium sulphide on phosphorus pentasulphide the compound $Ba_3(PS_4)_2$.aq. has been prepared in microscopic needles.[2]

Barium Selenophosphates.—By the action of phosphorus pentaselenide on barium hydroxide, or by saturating a barium hydroxide solution with hydrogen selenide, a white microcrystalline powder of composition $BaHSe_2O_2.14H_2O$ is obtained.[4]

Barium Azophosphates, or Phosphimates.—Certain compounds have been obtained containing both phosphorus and nitrogen. The following formulæ have been ascribed to them : $Ba_3P_2N_2O_8.2H_2O$,[5] $Ba_2H_4P_4N_4O_8.2H_2O$,[6] $BaNaH_3P_3N_3O_6.1\frac{1}{2}H_2O$,[7] and also a sulphur compound, $BaNPS_2.H_2O$.[5]

BARIUM AND ARSENIC.

Barium Arsenide, Ba_3As_2.—Soubeiran obtained a little arsenide mixed with arsenite by passing hydrogen arsenide over barium oxide at red heat.[8] It may be prepared by the reduction of barium arsenate with carbon in the electric furnace.[9]

Barium arsenide is slightly darker and more fusible than the other alkaline earth arsenides. Its density is 4·1 at 15° C. Its properties are somewhat similar to those of the other alkaline earth arsenides, but it is more reactive. It burns in fluorine, chlorine, and even bromine, without the application of heat. In oxygen it burns at about 300° C., and in sulphur vapour at dull red heat.

Barium Arsenites.—Barium Orthoarsenite, $Ba_3(AsO_3)_2$, is obtained as a white amorphous powder by precipitating barium chloride solution with potassium orthoarsenite and drying at 100° C. in a current of hydrogen. Addition of barium hydroxide solution does not give a pure compound.[10] An acid salt, $BaH_4(AsO_3)_2$, has also been described.[11]

[1] Ephraim and Majler, *Ber.*, 1910, **43**, 285.
[2] Ephraim and Stein, *ibid.*, 1911, **44**, 3405.
[3] Stock, *ibid.*, 1906, **39**, 2004.
[4] Ephraim and Majler, *ibid.*, 1910, **43**, 277.
[5] Gladstone, *Annalen*, 1850, **76**, 84 ; 1851, **77**, 317; see also Mente, *ibid.*, 1888, **248**, 232.
[6] Stokes, *Amer. Chem. J.*, 1896, **18**, 787.
[7] Stokes, *ibid.*, 1896, **18**, 645.
[8] Soubeiran, *Ann. Chim. Phys.*, 1830, [2], **43**, 415.
[9] Lebeau, *ibid.*, 1902, [7], **25**, 470 ; *Compt. rend.*, 1899, **129**, 47.
[10] Stavenhagen, *J. prakt. Chem.*, 1895. [2], **51**, 17.
[11] Bloxam, *J. Chem. Soc.*, 1862, **15**, 281.

Barium Pyroarsenite, $Ba_2AsO_5.2H_2O$, is prepared by precipitation from solutions of arsenious acid and barium hydroxide. The precipitate is dried at 100° C. If air-dried, the compound contains 8 molecules of water, according to Stavenhagen,[1] and 4 according to Stein.[2] When the salt is strongly heated, arsenic sublimes and barium arsenate is left.[2] Precipitation of barium chloride solution with potassium pyroarsenite also gives the pyroarsenite.[3]

Barium Metarsenite, $Ba(AsO_2)_2$, may be obtained by warming barium chloride with a solution of ammonium arsenite to which acetic acid has been added until arsenious acid is on the point of precipitation. The precipitate is then dried at 100° C.[1] It is a white powder easily soluble in water, but it can also be obtained as a gelatinous precipitate when a mixture of barium chloride and acid potassium arsenite in solution is left to stand a few hours.[3]

Barium Orthoarsenates.—*Tribarium Orthoarsenate*, $Ba_3(AsO_4)_2$, is formed in large colourless plates when barium oxide is fused with sodium or potassium orthoarsenate and chloride.[4] A trihydrate, $Ba_3(AsO_4)_2.3H_2O$, is prepared by precipitating excess of barium chloride solution with sodium arsenate, either cold or warm. A lower hydrate, $2Ba_3(AsO_4)_2.3H_2O$, which still retains its water at 130° C., has been mentioned.[5]

Barium chlorarsenoapatite, $3Ba(AsO_4)_2.BaCl_2$, can be obtained by fusing a mixture of barium oxide, an alkali chloride, and potassium or sodium metarsenate containing more than 60 per cent. of the latter.[6] Bromine and iodine arsenoapatites are also known.[7]

The double salts, $BaKAsO_4$[4] and $BaNH_4AsO_4.\frac{1}{2}H_2O$,[8] have been prepared.

Dibarium Orthoarsenate, $BaHAsO_4.H_2O$, or barium haidingerite, may be obtained by treating a fused mixture of barium oxide and potassium metarsenate with water,[9] or by the action of disodium hydrogen arsenate on a hot solution of barium chloride. The precipitate may be dried at 100° C.,[10] but loses half its water at 120° C. It is slightly soluble in both precipitants.[5] It forms transparent rhombic plates of density 3·926 at 15° C.[11] From acetic acid it may be recrystallised in the form of octahedra.[12]

A double salt, $Ba(NH_4)_2H_2(AsO_4)_2$, has been obtained.[8]

Monobarium Orthoarsenate is obtained by dissolving the di- or tri-barium compound in arsenic acid and evaporating.

Barium Pyroarsenate, $Ba_2As_2O_7$, is obtained by fusing barium oxide with potassium or sodium metarsenate and extracting with anhydrous glycerol.[9] In contact with cold water the hexahydrate, $Ba_2As_2O_7.6H_2O$, is formed.[4] The same crystals are obtained by

[1] Stavenhagen, *J. prakt. Chem.*, 1895, [2], **51**, 17.
[2] Stein. *Annalen*, 1850, **74**, 218.
[3] Filhol, *ibid.*, 1848, **68**, 310.
[4] Lefèvre, *Ann. Chim. Phys.*, 1892, [6], **27**, 17.
[5] Salkowski, *J. prakt. Chem.*, 1868, [1], **104**, 129.
[6] Lefèvre, *Compt. rend.*, 1889, **108**, 1058; *Ann. Chim. Phys.*, 1892, [6], **27**, 17.
[7] Ditte, *Ann. Chim. Phys.*, 1886, [6], **8**, 522, 529.
[8] Abegg, *Handbuch d. anorg. Chem.* (Hirzel, Leipzig), 1907, III Bd., 3 Abt., p. 541.
[9] Lefèvre, *Compt. rend.*, 1889, **108**, 1058.
[10] Kotschoubey, *Annalen*, 1850, **76**, 249.
[11] de Schulten, *Bull. Soc. franç. Min.*, 1904, **27**, 104.
[12] Schiefer, *Jahresber.*, 1864, 237.

precipitation from barium chloride and sodium arsenate solutions.[1] With boiling water, barium orthoarsenate is left as a solid, and the solution, on evaporation and calcination, gives barium metarsenate, $Ba(AsO_3)_2$.[1]

Barium Thioarsenites.—A number of thioarsenites can be obtained by the action of barium hydrosulphide on arsenic trisulphide under different conditions.[2] The following may be mentioned:— $BaS.As_2S_3.2H_2O$, $BaS.6As_2S_3$, $2BaS.As_2S_3.2H_2O$, in two forms, one grey-green and the other indigo-blue, $2BaS.As_2S_3$, $2BaS.As_2S_3.15H_2O$, $Ba_3(AsS_3)_2$ a white crystalline compound insoluble in alcohol, $Ba_3(AsS_3)_2.14H_2O$, and the pyrothioarsenite, $Ba_2As_2S_5$, forming a brown-red gummy substance very soluble in water. There is also a thio-oxyarsenite, $5BaS.2As_2S_2O.6H_2O$.[3]

Barium Thioarsenates. — Normal barium orthothioarsenate, $Ba_3As_2S_6.6H_2O$, is formed by the action of barium hydrosulphide on arsenic pentasulphide as faintly yellow, thick, transparent needles. It is only slightly soluble in water, by which it is decomposed. When it is heated, water of crystallisation is given off and the colour deepens. At higher temperatures it is decomposed.[1] A pyrothioarsenate has been isolated.[2] There are also oxy-compounds, for example $Ba_3(AsOS_3)_2.5H_2O$,[5] and $Ba_3(AsO_3S)_2.6H_2O$,[6] $Ba_3(AsO_2S_2)_2.7H_2O$,[7] and double salts, $BaKAsS_4.6H_2O$,[6] $BaNaAsO_3S.9H_2O$,[7] $BaKAsOS_3.7H_2O$,[5] and $Ba_7Na_2As_5S_{14}O_7.12H_2O$.[5]

Barium Sodium Selenoxyarsenate.—A compound of formula $BaNaAsO_3Se.9H_2O$ has been isolated.[6]

BARIUM AND ANTIMONY.

Barium Metantimonate, $Ba(SbO_3)_2.5H_2O$,[9] or $6H_2O$,[10] is obtained as a white crystalline compound insoluble in water by the action of sodium antimonate on a solution of a barium salt.[11] A slightly basic compound is also known, $Ba(OH)_2.12(BaO.Sb_2O_5.6H_2O)$.[10]

Barium Thioantimonites.—By the action of solutions of barium hydrosulphide and sulphide on antimony trisulphide the following compounds may be obtained : the orthothioantimonite, $Ba_3Sb_2S_6.8H_2O$, in golden-yellow crystals, the grey-green pyrothioantimonite, $Ba_2Sb_2S_5.8H_2O$, and a chestnut-brown compound of the formula $Ba_3Sb_4S_9.10H_2O$.[12]

Barium Chloroantimonite, $SbCl_3.2BaCl_2.5H_2O$.[13]

Barium Orthothioantimonate, $Ba_3Sb_2S_8.6H_2O$, is formed, as bright yellow crystals soluble in water, by the action of barium hydrosulphide on antimony pentasulphide. By adding a large excess of potassium

[1] Lefèvre, *Ann. Chim. Phys.*, 1892, [6], **27**, 17.
[2] Nilson, *J. prakt. Chem.*, 1876, [2], **14**, 44
[3] Nilson, *ibid.*, 1877, [2], **16**, 93.
[4] Glatzel, *Zeitsch. anorg. Chem*, 1911, **70**, 86.
[5] McCay and Foster, *ibid.*, 1904, **41**, 464.
[6] Weinland and Rumpf, *ibid.*, 1897, **14**, 42.
[7] McCay, *Chem. Zeit.*, 1897, **21**, 487.
[8] Glatzel, *Zeitsch. anorg. Chem.*, 1911, **71**, 209.
[9] Ebel, *Ber.*, 1889, **22**, 3044.
[10] Hoffter, *Pogg. Annalen*, 1852, 86, 418.
[11] Ebel, *loc. cit.* ; Hoffter, *loc. cit.*
[12] Pouget, *Compt. rend.*, 1898, **126**, 1792.
[13] Poggiale, *ibid.*, 1845, **20**, 1182.

chloride to the solution the compound $KBaSbS_4.6H_2O$, or K_3SbS_4.$Ba_3(SbS_4)_2.18H_2O$, is obtained as colourless crystals which darken on exposure to air. When heated they melt and lose water.[1]

BARIUM AND VANADIUM.

Barium Hypovanadate, $BaV_4O_9.4H_2O$, or vanadite, as it is called, although it does not correspond to the phosphites, is obtained as a brownish-yellow precipitate, rather insoluble in water, by the addition of barium hydroxide solution to a vanadyl salt.[2]

Barium Vanadates.—Barium orthovanadate cannot be separated because on formation it splits up immediately into barium hydroxide and pyrovanadate.[3] Barium pyrovanadate, $Ba_2V_2O_7$, is obtained by the precipitation of barium chloride by sodium ortho- or pyro-vanadate.[4] It is slightly soluble in water.

Barium metavanadate, BaV_2O_6, is obtained in the form of yellowish transparent crystals, slightly soluble in water, by heating sodium and barium bromide with vanadic acid,[5] or in colourless transparent prisms, insoluble in water, by adding barium nitrate in excess to a boiling solution of ammonium vanadate.[6] A monohydrate, $BaV_2O_6.H_2O$, is formed as a flocculent, yellowish-white precipitate by the action of the normal potassium or ammonium[7] salt on barium chloride solution. On long standing, or on drying, it becomes crystalline. It loses practically all its water at 180°–200° C. After fusion it solidifies to a brownish-yellow glass.[8]

Certain acid salts are known, $2BaO.3V_2O_5.14H_2O$, obtained in orange-red, transparent, rhombic crystals by the action of a boiling solution of ammonium vanadate on excess of barium nitrate in the presence of acetic acid,[6] and $3BaO.5V_2O_5.19H_2O$.[9]

Halogen compounds corresponding to the apatites and wagnerites have been obtained.[10]

Barium fluoroxyvanadate, $BaF_2.VO_2F$, is formed as a heavy, bright yellow, insoluble powder by precipitating barium fluoride with potassium fluoroxyvanadate.[11]

Barium Metapervanadate, $Ba(VO_4)_2$, is obtained as a heavy, amorphous, yellow precipitate by the action of a saturated solution of ammonium metapervanadate in 30–33 per cent. hydrogen peroxide, free from sulphuric acid, on barium chloride solution. After washing with hydrogen peroxide it is dried over calcium chloride.[12]

[1] Glatzel, *Zeitsch. anorg. Chem.*, 1911, **72**, 100.
[2] Koppel and Goldmann, *ibid.*, 1903, **36**, 300; see also Crow, *J. Chem. Soc.*, 1876, **30**, 453, who assigns to it 5H₂O.
[3] Manasse, *Annalen*, 1887, **240**, 23.
[4] Roscoe, *J. Chem. Soc.*, 1871, **24**, 23; see also Berzelius, *Pogg. Annalen*, 1831, **22**, 46.
[5] Ditte, *Compt. rend.*, 1883, **96**, 1048.
[6] Ditte, *ibid.*, 1887, **104**, 1705.
[7] Berzelius, *loc. cit.*
[8] Ditte, *Ann. Chim. Phys.*, 1886, [6], **8**, 502; Manasse, *loc. cit.*
[9] Berzelius, *loc. cit.*; von Hauer, *Sitzungsber. K. Akad. Wiss. Wien*, 1856, **21**, 333; *J. prakt. Chem.*, 1860, [1], 80, 324, Manasse, *loc. cit.*; Norblad, *Ber.*, 1875, 8, 126; Guyard, *Bull. Soc. chim.*, 1876, [2], **25**, 58, 351; Rosenheim, *Zeitsch. anorg. Chem.*, 1916, **96**, 139.
[10] Ditte, *Ann. Chim. Phys.*, 1886, [6], **8**, 502; *Compt. rend.*, 1883, **96**, 846, 1226.
[11] Ephraim, *Zeitsch anorg. Chem.*, 1903, **35**, 79.
[12] Scheuer, *ibid.*, 1898, **16**, 284.

BARIUM AND COLUMBIUM.

Barium Columbate.—The compound, $7BaO.6Cb_2O_5.18H_2O$, forms a thick white precipitate when the corresponding sodium salt is treated with barium chloride.[1]

A columboxalate, $5BaO.Cb_2O_5.10C_2O_3.20H_2O$, is precipitated by the action of a solution of a barium salt on the potassium salt, $3K_2O.Cb_2O_5.6C_2O_3$, or by digesting a mixture of barium oxalate and hydrated columbic acid with oxalic acid. It forms crystals insoluble in water, hydrochloric acid, and nitric acid. By hot acids it is decomposed, giving columbic acid. It is soluble in warm oxalic acid solution.[2]

BARIUM AND TANTALUM.

Barium Tantalate.—By the action of the corresponding alkali salt on a soluble barium salt, barium hexatantalate, $4BaO.3Ta_2O_5.6H_2O$, is obtained as a voluminous white precipitate. On being heated the salt shows strong luminescence.[3]

Barium Pertantalate.—By the action of potassium pertantalate on barium chloride in aqueous solution, a white voluminous precipitate is obtained. It is decomposed by carbon dioxide, forming hydrogen peroxide.[1]

BARIUM AND CARBON.

Barium Carbide, BaC_2, was first obtained in an impure form by reducing barium carbonate with magnesium in the presence of carbon,[5] or by heating a mixture of barium amalgam with powdered carbon in a current of hydrogen at red heat.[6] The pure compound is prepared as a black crystalline mass, of density 3·75, by reducing anhydrous barium oxide or barium carbonate with carbon in the electric furnace,[7] or with the oxyhydrogen flame.[8] Its properties are similar to those of the other alkaline earth carbides, but it is more fusible. It reacts with sulphur, selenium, arsenic, phosphorus, chlorine, iodine, bromine, and oxygen.

It dissociates at high temperatures, the metal volatilising and leaving crystals of graphite.[9] When strongly heated in the electric furnace, barium carbide can be made to take up carbon in solution.[10]

Barium Carbonyl, $Ba(CO)_2$, is obtained as a yellow solid by the action of carbon monoxide on a solution of barium ammonium in ammonia. It is decomposed by contact with air, by heat, or by solution in water.[11]

Barium Formate, $Ba(HCOO)_2$, is obtained by mixing barium hydroxide and formic acid solutions and allowing to crystallise. It

[1] Bedford, *J. Amer. Chem. Soc.*, 1905, **27**, 1216.
[2] Russ, *Zeitsch. anorg. Chem.*, 1902, **31**, 74.
[3] Rose, *Jahresber.*, 1857, 182.
[1] Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.*, 1899, **20**, 347.
[5] Maquenne, *Ann. Chim. Phys.*, 1893, [6], **28**, 259.
[6] Maquenne, *Compt. rend.*, 1892, **114**, 361 ; *Ann. Chim. Phys*, 1893, [6], **29**, 223.
[7] Moissan, *Electric Furnace*, English translation (Williams & Norgate), 1908; *Compt. rend.*, 1894, **118**, 683.
[8] Kahn, *Compt. rend.*, 1907, **144**, 913.
[9] Gin and Leleux, *ibid.*, 1898, **126**, 749.
[10] Kahn, *ibid.*, 1907, **144**, 197.
[11] Mentrel, *ibid.*, 1902, **135**, 740.

forms monoclinic prisms.[1] It is very soluble in water, but the solubility values obtained are not concordant.[2] It is practically insoluble in alcohol, 100 grm. of the latter only dissolving 0·0063 grm. of the salt.[3] The freezing-point lowering in aqueous solution, and hence the degree of dissociation at different concentrations, has been determined,[1] and also the refractive index in the solid state and in solution.[5] The density of the solid salt is 3·212.[6]

There is a double salt with copper, $2Ba(HCOO)_2.Cu(HCOO)_2.2H_2O$, forming bright blue crystals of density 2·747.[6]

Barium Acetate, $Ba(CH_3COO)_2$, crystallises from solutions of barium hydroxide in acetic acid at 0° C. in monoclinic crystals with 3 molecules of water, and above 10° C. in flattened triclinic prisms with 1 molecule. It is dehydrated at 130°–140° C., forming a snow-white hard powder of density 2·440.[7] Sharp breaks in the solubility curve, as well as dilatometric determinations, indicate transition points at 24·7° C. and 41° C.[8]

Aqueous solutions have been studied from the point of view of density,[9] freezing-point lowering,[1] and electrical conductivity.[10]

The solubility in alcohol is only slight, 0·0385 grm. in 100 grm. of solvent.[11]

Acid salts of composition $3Ba(CH_3COO)_2.3CH_3COOH.11H_2O$, and $Ba(CH_3COO)_2.2CH_3COOH$, have been obtained.[12] A compound, $BaCl_2.Ba(CH_3COO)_2.2CH_3COOH$, is also known, or, preferably, on account of its behaviour, $BaCl(CH_3COO).CH_3COOH$.[13]

Barium Oxalate, BaC_2O_4, may be obtained by precipitation of a soluble barium salt with a soluble oxalate, or by the action of oxalic acid on barium hydroxide. There are apparently three hydrates, containing 3·5, 2, and 0·5 molecules of water of crystallisation respectively. From solubility determinations it may be concluded that the first is stable below 0° C., the second between 0° and 10° C., and the third above 40° C.[14]

Kohlrausch determined the solubility by electrical conductivity measurements, and obtained values which differed somewhat according to the conditions of preparation. The average value, however, was 0·785 milli-equivalents, or 0·088 grm. per litre calculated as anhydrous salt.[15] The solubility is greater in acetic acid than in water, the maximum being reached in approximately $4N$ acid.[16]

[1] Stanley, *Chem. News*, 1904, **89**, 193.
[2] Plathan, *Dissertation*, Helsingfors, 1897; Krasicki, *Monatsh.*, 1897, **8**, 595; Stanley, *loc. cit.*
[3] Haberland, *Zeitsch. anal. Chem.*, 1899, **38**, 221; see also Stanley, *loc. cit.*
[4] Calame, *Zeitsch. physikal. Chem.*, 1898, **27**, 401.
[5] Kannonikow, *J. prakt. Chem.*, 1885, [2], **31**, 321.
[6] Schroder, *Ber.*, 1881, **14**, 21.
[7] Schröder, *ibid.*, 1879, **12**, 564.
[8] Walker and Fyffe, *Trans. Chem. Soc.*, 1903, **83**, 173.
[9] Franz, *J. prakt. Chem.*, 1872, [2], **5**, 298; see Gerlach, *Zeitsch. anal. Chem.*, 1888, **27**, 289.
[10] MacGregory, *Wied. Annalen*, 1894, **51**, 126; Kohlrausch and Holborn, *Leitvermögen der Elektrolyte* (B. G. Teubner, Leipzig), 1898.
[11] Haberland, *loc. cit.*
[12] Iwaki, *Mem. Coll. Sci. Kyoto*, 1914, **1**, 81, see *J. Chem. Soc.*, 1915, **108**, Abs. i, 492.
[13] Colson, *Compt. rend.*, 1903, **137**, 660.
[14] Groschuff, *Ber.*, 1901, **34**, 3313, but see Souchay and Lenssen, *Annalen*, 1856, **99**, 31.
[15] Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, **64**, 129; see also 1893, **12**, 234; 1904, **50**, 355.
[16] Herz and Muhs, *Ber.*, 1903, **36**, 3715.

An acid salt, barium binoxalate, $Ba(HC_2O_4)_2$, may be prepared in the anhydrous state, or with 1 or 2 molecules of water of crystallisation.[1] It is more soluble in water than the neutral salt, and is decomposed by water unless excess of oxalic acid is present.[2] For any one temperature there must naturally be a definite concentration in acid salt if both the solid phases, neutral salt and acid salt are present.

Barium Carbonate, $BaCO_3$, occurs naturally as the mineral *witherite*, in orthorhombic crystals isomorphous with aragonite and strontianite. A mineral consisting of mixed crystals of barium and calcium carbonates, *barytocalcite*, is also found.

Barium carbonate may be readily obtained by precipitation from a solution of a barium salt by an alkali carbonate, or by the action of carbon dioxide on barium hydroxide solution. It can be formed by the union of carbon dioxide with anhydrous barium oxide if the temperature is raised to about 550° C.[3] It may also be obtained in crystalline form by fusion of barium chloride with sodium carbonate and extraction with water, or by fusion of the precipitated carbonate with sodium chloride,[4] or by heating with ammonium nitrate or carbonate solution in a sealed tube at 150°–180° C.[5]

Commercially it is prepared from the sulphate by reduction to the sulphide and treatment of a hot solution of the latter with carbon dioxide.[6]

The density of witherite is 4·3–4·5, and of the precipitated carbonate 4·22–4·37.[7] The specific heat is 0·14483.[8]

Barium carbonate is more difficult to decompose than either calcium or strontium carbonate. The dissociation pressure only reaches one atmosphere at 1350° C.,[9] when, according to Finkelstein, a basic carbonate, $BaO.BaCO_3$, is formed.[10] This basic carbonate melts below 950° C. It can be formed by prolonged heating at 1120° C., and it dissolves barium oxide and, at higher temperatures, barium carbonate. By extrapolation the temperature of decomposition of the basic carbonate is found to be 1454° C.

Le Chatelier gave the temperature of fusion in an open vessel as 795° C.,[11] but this low value was no doubt due to the formation of barium oxide. It only partially fuses when heated at 1380° C. in a current of carbon dioxide. The melting-point under a pressure of carbon dioxide appears to be about 1740° C., when determined by extrapolation from the fusion curve of mixtures of calcium and barium carbonates. There are two transition points, one at 811° C., from witherite or γ-carbonate to β-carbonate, a hexagonal form, and the other at

[1] Souchay and Lenssen, *loc. cit.* ; Loschmidt, *Jahresber.*, 1865, 375.

[2] Groschuff, *loc. cit.*

[3] Raoult, *Compt. rend.*, 1881, **92**, 1110.

[4] Bourgeois, *Ann. Chim. Phys.*, 1883, [5], **29**, 486.

[5] Bourgeois, *Bull. Soc. chim.*, 1887, [2], **47**, 81.

[6] Rivière, *Bull. Soc. Mulh.*, 1866, **36**, 438 ; Scheurer-Kestner, *ibid.*, 448 ; see also Lieber, *Dingl. poly. J.*, 1883, **250**, 69.

[7] Schröder, *Jahresber.*, 1859, 12.

[8] Regnault, *Ann. Chim. Phys.*, 1841, [3], **1**, 182.

[9] Johnston, *J. Amer. Chem. Soc.*, 1908, **30**, 1357 ; *Zeitsch. anorg. Chem.*, 1908, **62**, 330 ; see also Herzfeld and Stiepel, *Chem. Zentr.*, 1898, ii, 1197 ; de Forcrand, *Compt. rend.*, 1908, **146**, 511 ; Brill, *Zeitsch. anorg. Chem.*, 1905, **45**, 282 ; Finkelstein, *Ber.*, 1906, **39**, 1585 ; Hedvall found 1361° C., *Zeitsch. anorg. Chem.*, 1916, **98**, 53.

[10] Finkelstein, *loc. cit.*

[11] Le Chatelier, *Bull. Soc. chim.*, 1887, [2], **47**, 300

982° C., from β- to α-barium carbonate, which is regular in crystalline form.[1]

If carbon dioxide be passed through a methyl alcoholic solution of barium oxide, barium carbonate separates in a gelatinous form and behaves as a reversible colloid, giving a clear solution which is practically a non-conductor of electricity so long as it is not completely freed from methyl alcohol.[2]

By the action of sodium on barium carbonate, carbon is liberated and the oxide formed.[3] Carbon also separates when a solid mixture of chloride and carbonate is electrolysed at 550°–600° C.[3]

The solubility of barium carbonate in water is very small, but greater than that of the other alkaline earth carbonates. The results obtained by different investigators are rather variable, as the solubility depends on the pressure of carbon dioxide, and there are probably present in solution hydroxyl ions due to the hydrolysis of the salt, and hydrogen carbonate ions owing to the formation of bicarbonate. By electrical conductivity determinations the solubility was found to be 24 mgm., or 1.22×10^{-4} grm.-mol. per litre at 18° C.[4] Weissenberger determined the solubility in the presence of a small quantity of caustic soda to suppress the hydrolysis, and observed a minimum solubility at a hydroxyl-ion concentration of 1.25×10^{-5} grm.-ion per litre.[5] With a higher concentration the hydroxide is formed, and therefore the solubility is apparently increased. The true values of the solubility were considered to be as follows :—

Temperature °C.	14	18	23	27	32	38
Gram-molecules $BaCO_3$ per litre $\times 10^4$	4.32	4.57	4.89	5.22	5.69	6.27

The solubility is increased by the presence of ammonium chloride,[6] probably due to the formation of a double chloride in solution,[7] and also by potassium and sodium chlorides and sulphates, magnesium and zinc sulphates, and by calcium nitrate and chloride, all of which probably bring about partial decomposition of the carbonate.[8]

McCoy and Smith, working under pressures of 0.2–30 atmospheres of carbon dioxide, found as the value of the solubility product $[Ba^{..}] \times [CO_3'']$, 8.1×10^{-9} at 25° C.[9] The maximum solubility was reached at 22 atmospheres and was 7.3 grm. of barium bicarbonate per litre at 25° C. Above this pressure, therefore, it should be possible to separate the solid bicarbonate. This compound may apparently be precipitated from ice-cold solutions of barium chloride by ammonium

[1] Boeke, *Zeitsch. anorg. Chem.*, 1906, 50, 244 ; *Chem. Zentr.*, 1913, 1, 1909.

[2] Neuberg and Neimann, *Biochem. Zeitsch.*, 1906, 1, 166 ; Neuberg and Rewald, *ibid.*, 1908, 9, 538.

[3] Haber and Tolloczko, *Zeitsch. anorg. Chem.*, 1904, 41, 412.

[4] Kohlrausch and Rose, *Zeitsch. physikal. Chem.*, 1893, 12, 241 ; 1903, 44, 197 ; see also Gardner and Gerassimoff, *ibid.*, 1904, 48, 359 ; Holleman, *ibid.*, 1893, 12, 135.

[5] Weissenberger, *Zeitsch. physikal. Chem.*, 1914, 88, 257 ; see also Kuster, *Zeitsch. anorg. Chem.*, 1900, 22, 161 ; Bodländer, *Zeitsch. physikal. Chem.*, 1900, 35, 23 ; Gardner and Gerassimoff, *loc. cit.*

[6] Vogel, *J. prakt. Chem.*, 1836, [1], 7, 453 ; Wackenroder, *Annalen*, 1842, 41, 315.

[7] Kernot, d'Agostino, and Pellegrino, *Gazzetta*, 1908, 38, i, 532.

[8] See Cantoni and Goguélia, *Bull. Soc. chim.*, 1905, [3], 33, 13.

[9] McCoy and Smith, *J. Amer. Chem. Soc.*, 1911, 33, 468 ; but see Bodländer, *Zeitsch. physikal. Chem.*, 1900, 35, 23 ; see also Schlösing, *Compt. rend.*, 1872, 75, 70.

bicarbonate, preferably with the addition of gelatine to stabilise it,[1] its composition being approximately represented by the formula $BaCO_3.1\cdot5H_2CO_3$.[2] A compound of composition $2BaO.3CO_2$ was described by Boussingault as formed by the action of sodium sesquicarbonate on barium chloride.[3]

A double salt with potassium carbonate, $BaCO_3.K_2CO_3$, is formed by precipitation from saturated solutions of barium chloride and potassium carbonate at room temperature.[4] The same compound, as well as a similar sodium salt, may also be formed by fusion.[5]

Barium Thiocarbonate, $BaCS_3$, is obtained as a yellow microcrystalline product by the action of carbon disulphide on barium hydrosulphide,[6] sulphide,[7] or hydroxyhydrosulphide,[8] in a current of hydrogen. It is more stable than the other alkaline earth thiocarbonates, is insoluble in alcohol, and slightly soluble in water, forming a red solution which dissolves one atom of sulphur per molecule of salt. No solid perthiocarbonate has, however, been isolated. On evaporation of the solution, oxidation takes place with the formation of barium thiosulphate.[9] It is also obtained in a hydrated form, crystallising in short prisms, by the action of sunlight on barium hydroxide and carbon disulphide in the presence of water.

Barium Percarbonate, $BaCO_4.aq.$, is obtained as a light yellow compound by cooling a suspension or solution of barium peroxide to $0°$ C. and treating with carbon dioxide, the peroxide being always in excess.[10] It is hydrated, and is not to be regarded as $BaCO_3.H_2O_2$, because neither alcohol nor ether extracts hydrogen peroxide from it, and it only gives up hydrogen peroxide slowly on treatment with water. It is a convenient reagent for the preparation of neutral hydrogen peroxide by treatment either with water or with an acid producing an insoluble barium salt.

Barium Cyanide, $Ba(CN)_2$, is formed by passing anhydrous hydrocyanic acid over cooled barium hydroxide crystals, and dissolves in the water of crystallisation of the hydrated baryta. With anhydrous barium oxide or hydroxide too vigorous a reaction takes place and the cyanide is decomposed. Prismatic crystals of the dihydrate, $Ba(CN)_2.2H_2O$,[11] may be obtained by adding a slight excess of hydrocyanic acid and evaporating *in vacuo* in presence of sulphuric acid and a small quantity of caustic potash. They are deliquescent and readily decomposed by the carbon dioxide of the air. Over sulphuric acid *in vacuo* the more stable monohydrate is obtained, and this may be completely dehydrated by a slow current of dry air, first at $75°$ C., and then at $100°$ C. The anhydrous salt is white and very hygroscopic. It is also very soluble in water, eight parts dissolving in ten of water,

[1] Keiser and McMaster, *J. Amer. Chem. Soc.*, 1908, **30**, 1714.
[2] Keiser and Leavitt, *ibid.*, 1908, **30**, 1711.
[3] Boussingault, *Ann. Chim. Phys.*, 1825, [2], **29**, 288.
[4] Datta and Mukherjea, *Proc. Chem. Soc.*, 1913, **29**, 185 ; but see Barre, *Compt. rend.*, 1912, **154**, 279.
[5] Le Chatelier, *Compt. rend.*, 1894, **118**, 415.
[6] Yeoman, *Trans. Chem. Soc.*, 1921, **119**, 48.
[7] Thénard, *Compt. rend.*, 1874, **79**, 673 ; Berzelius, *Pogg. Annalen*, 1826, **6**, 444.
[8] Veley, *Trans. Chem. Soc.*, 1886, **49**, 378.
[9] Yeoman, *loc. cit.* ; see also Veley, *loc. cit.* ; Thénard, *loc. cit*
[10] Wolffenstein and Peltner, *Ber.*, 1908, **41**, 275.
[11] Meitzendorff, *Pogg. Annalen*, 1842, **56**, 69.

and fairly soluble in alcohol. The heat of hydration to the mono-hydrate is 1·94 Cal., and to the dihydrate 3·17 Cal.[1]

Barium cyanide is also formed by the action of carbon monoxide on barium nitride,[2] by the calcination of barium ferrocyanide and extraction with water,[3] and by the action of cyanogen gas on barium amalgam.[4] Pure barium cyanide may be prepared by suspending finely powdered barium hydroxide in light petroleum and adding an emulsion of anhydrous hydrocyanic acid in light petroleum.[5] It fuses at about 600° C. and is rather volatile.

By passing nitrogen over barium carbide heated to redness in iron retorts, about 30 per cent. of the carbide is converted into cyanide, the rest forming barium cyanamide. By fusing with sodium carbonate the remainder of the carbon is taken up and cyanide formed.[6]

When the cyanide is heated to 300° C. in the presence of steam the whole of the nitrogen is evolved in the form of ammonia, leaving barium formate,[7]

$$Ba(CN)_2 + 4H_2O = Ba(HCOO)_2 + 2NH_3.$$
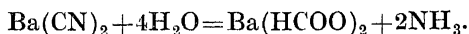
The compound $Ba(CN)(OCH_3).CH_3OH$ is obtained when hydrocyanic acid is passed into a methyl alcohol solution of barium oxide. It loses alcohol at 100° C., and at still higher temperatures forms the basic cyanide, $BaO.Ba(CN)_2$.[4]

Aqueous solutions of barium cyanide dissolve insoluble cyanides of some of the heavy metals forming crystalline double salts—for example, $BaHg(CN)_4.3H_2O$ in needles,[8] $2Ba(CN)_2.3Hg(CN)_2.23H_2O$ in transparent octahedra,[9] and $Ba(CN)_2.Hg(CN)_2.HgI_2.6H_2O$;[10] barium manganocyanide, $Ba_2Mn(CN)_6$,[11] barium manganicyanide, $Ba_3[Mn(CN)_6]_2$,[12] barium manganese manganocyanide, $BaMn[Mn(CN)_6]$,[13] and also a double manganocyanide of barium and potassium ;[13] barium cobaltocyanide, $Ba_2Co(CN)_6$, and an unstable barium chromocyanide,[13] and also a barium ruthenocyanide, $Ba_2Ru(CN)_6.6H_2O$.[14]

Barium Cyanamide, BaCN₂.—The formation of barium cyanamide along with cyanide by the action of nitrogen on barium carbide has already been mentioned. Absorption readily takes place at 700°–800° C.[15] A mixture of barium carbonate, or oxide, and carbon can be

[1] Joannis, *Ann. Chim. Phys.*, 1882, [5], **26**, 482.

[2] Maquenne, *Compt. rend.*, 1892, **114**, 220 , *Bull. Soc. chim.*, 1892, [3], **7**, 366.

[3] Schulz, *J. prakt. Chem.*, 1856, [1], **68**, 257 ; see also Ewan and Napier, *J. Soc. Chem. Ind.*, 1913, **32**, 467.

[4] Drechsel, *J. prakt. Chem.*, 1880, [2], **21**, 77.

[5] Ewan and Napier, *loc. cit.*

[6] Erlwein, *Zeitsch. angew. Chem.*, 1903, **16**, 533 ; Margueritte and Sourdeval, *Compt. rend.*, 1860, **50**, 1100.

[7] Margueritte and Sourdeval, *loc. cit.*; Rolla, *Ann. Chim. applicata*, 1914, **2**, 301, see *J. Chem. Soc.*, 1915, **108**, Abs. i, 58.

[8] Grossman and von der Forst, *Ber.*, 1904, **37**, 4141

[9] Jackson, *Pharm. Centr.*, 1836, **1**, 350.

[10] Varet, *Compt. rend.*, 1895, **121**, 499.

[11] Eaton and Fittig, *Annalen*, 1868, **145**, 157 ; Descamps, *Ann. Chim. Phys.*, 1881, [5], **24**, 178.

[12] Eaton and Fittig, *loc. cit.*

[13] Descamps, *loc. cit.*

[14] Howe, *J. Amer. Chem. Soc*, 1896, **18**, 986. For barium platinocyanide and ferro- and ferri-cyanides see Vol. IX. of this series, Parts I. and II. For further information on barium cyanide, see Williams, *The Chemistry of Cyanogen Compounds* (Churchill), 1915 ; Köhler, *Die Industrie der Cyanverbindungen* (Braunschweig), 1914 ; Rideal and Taylor, *Catalysis in Theory and Practice* (Macmillan & Co.), 1919, p. 246.

[15] Frank, *Trans. Faraday Soc.*, 1908, **4**, 99.

substituted for the carbide.[1] Absorption then begins a little above 900° C.[2] It is favoured by the presence of calcium chloride,[3] and addition of barium chloride seems to facilitate it a little at low temperatures, but to decrease it at high.[4] On the whole, barium chloride decreases the proportion of cyanamide.[4]

There seems to be doubt as to the effect of temperature on the relative proportions of the two substances formed. According to Kuhling and Berkhold the proportion of cyanamide decreases with rise of temperature,[4] but Ewan and Napier[2] found that fusion of barium cyanide results in the formation of barium cyanamide, the amount of the latter depending on the duration and temperature of heating, the presence of finely divided iron also increasing the proportion of cyanamide. This supports the statement of Askenasy and Grude that at 1300°–1400° C. cyanide is first formed, and this at still higher temperatures gives cyanamide, the latter process being also favoured by a shortage of carbon.[5] The equilibrium can no doubt be approached from either side, but the variation in the position of equilibrium with temperature has apparently not been very carefully studied. Fusion of the cyanide-cyanamide mixture with potash or soda also converts the whole into cyanide.[6]

Barium cyanamide may also be obtained by fusing barium cyanate.[7]

By passing carbon dioxide into an aqueous solution of barium cyanamide, prepared by dissolving barium hydroxide in a solution of cyanamide, filtering, and adding more cyanamide, a heavy, granular, crystalline precipitate of composition $2(BaCN_2.CO_2).3H_2O$ is readily obtained.[8]

Barium Cyanate, $Ba(CNO)_2$, may be prepared by adding alcohol to a solution of a mixture of potassium cyanate and barium acetate, or, more readily, by heating barium cyanurate until it melts, when it is converted into barium cyanate. The salt crystallises in prisms, and its solution decomposes on boiling with formation of urea and barium carbonate.[9]

$$Ba(CNO)_2 + 3H_2O = BaCO_3 + (NH_2)_2CO.$$
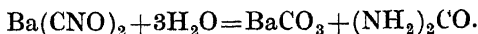
Barium Cyanurate.—An acid salt, $Ba[H_2(CNO)_3]_2.2H_2O$, may be prepared by the action of a hot solution of cyanuric acid on barium hydroxide. It is only completely dehydrated at 280° C. A salt with a neutral reaction, of composition $Ba_2[H(CNO)_3]_2.3H_2O$, is also obtained as a crystalline precipitate by the addition of cyanuric acid to an ammoniacal solution of barium chloride. It only begins to lose water at 200° C., and at higher temperatures it evolves ammonia and cyanic acid, leaving neutral barium cyanate.[10]

Barium Thiocyanate, $Ba(CNS)_2$, is prepared by boiling the cuprous or ammonium salt with barium hydroxide solution. It crystallises in long shining deliquescent needles with 2 molecules of water of

[1] Marguerittte and Sourdeval, *Compt. rend.*, 1860, 50, 1100 ; Kühling, *Ber.*, 1907, 40, 310 ; Askenasy and Grude, *Zeitsch. Elektrochem.*, 1922, 28, 130.
[2] Ewan and Napier, *J. Soc. Chem. Ind.*, 1913, 32, 467.
[3] Kühling, *loc. cit.*
[4] Kühling and Berkhold, *Ber.*, 1908, 41, 28.
[5] Askenasy and Grude, *loc. cit.*
[6] Frank, *loc. cit.*
[7] Drechsel, *J. prakt. Chem.*, 1877, [2], 16, 200.
[8] Meyer, *ibid.*, 1878, [2], 18, 419.
[9] O. and J. Masson, *Zeitsch. physikal. Chem.*, 1910, 70, 290.
[10] Wohler, *Annalen*, 1847, 62, 251.

crystallisation.[1]   It can also be formed by the action of thiocyanic acid on barium carbonate.

It loses its water of crystallisation at 120°–130° C., or at ordinary temperatures over sulphuric acid.[2]   It is very soluble in water, 100 c.c. of a solution saturated at 15° C. containing 103·7 grm. of the anhydrous salt.

Various double salts have been isolated—for example, $BaHg(CNS)_4$ and $Ba[Hg(CNS)_3]_2$,[3] $Ba(CNS)_2.2Hg(CNS)_2.4H_2O$,[4] $Ba(CNS)_2.Hg(CN)_2$, $Ba(CNS)_2.2HgBr_2.5H_2O$,   and $BaZn(CNS)_4.7H_2O$,[5] $Ba_3Cr_2(CNS)_{12}.$ $16H_2O$,[6] and $Ba[(CrNH_3)_2(CNS)_3]_2(CNS)_2$.[7]

Barium thiocyanate forms compounds with ethyl alcohol, $Ba(CNS)_2.$ $2C_2H_5OH$ and $Ba(CNS)_2.C_2H_5OH$, and also one with methyl alcohol, $Ba(CNS)_2.2CH_3OH$.[2]

Barium Selenocyanate has also been obtained by dissolving barium carbonate in selenocyanic acid.[8]

BARIUM AND SILICON.

Barium Silicide, $BaSi_2$, may be obtained similarly to the calcium and strontium silicides by reducing a mixture of barium oxide and silica by carbon in the electric furnace,[9] by heating together barium oxide and silicon,[10] or by combining barium and silicon directly.[11]   With dilute hydrochloric acid, silicon hydride is evolved and silica deposited. The physical and chemical properties of the compound are similar to those of strontium silicide, but the former is more readily attacked by reagents than the latter.

Barium Silicates.—Barium silicate occurs in nature under the form of various silico-aluminates, such as *harmotome, brewsterite,* and *barytafelspar.*

A barium orthosilicate, Ba_2SiO_4, melting at 1750° C., has been mentioned,[12] but it is probably not stable in contact with water.[13]

Barium metasilicate, $BaSiO_3$, may be formed by fusing a mixture of barium chloride and carbonate with silica.[14]   It may be obtained as the hydrate, $BaSiO_3.H_2O$, by precipitation of a soluble barium salt with an alkali silicate.[13]   A hexahydrate has also been described, prepared by the action of barium hydroxide solution on sodium silicate or colloidal silica.   The heat of reaction of dissolved barium hydroxide with colloidal silica is 8 Cal.   It is probably decomposed by water, but the decomposition is prevented by the presence of barium hydroxide

[1] Tcherniac, *Ber.,* 1892, **25**, 2627 ; Meitzendorff, *Pogg. Annalen,* 1842, **56**, 68.
[2] Tcherniac, *loc. cit.*
[3] Rosenheim and Cohn, *Ber.,* 1900, **33**, 1111.
[4] Böckmann, *Annalen,* 1877, **22**, 153 ; Clève, *Bull. Soc. chim.,* 1875, [2], **23**, 71.
[5] Williams, *The Chemistry of the Cyanogen Compounds* (Churchill), 1915, p. 194.
[6] Rössler, *Annalen,* 1867, **141**, 185.
[7] Nordenskjöld, *Zeitsch. anorg. Chem.,* 1892, **1**, 134.
[8] Crookes, *J. Chem. Soc.,* 1852, **4**, 19.
[9] Bradley, *Chem. News,* 1900, **82**, 149.
[10] Goldschmidt, *J. Chem. Soc.,* 1908, **94**, Abs. ii, 1037.
[11] Hönigschmid, *Monatsh.,* 1909, **30**, 497.
[12] Jäger and van Klooster, *Sprechsaal,* 1919, **52**, 256, see *J. Soc. Glass Tech.,* 1919, **3**, 234A.
[13] Jordis and Kanter, *Zeitsch. anorg. Chem.,* 1903, **35**, 82 ; 1904, **42**, 418.
[14] Bourgeois, *Ann. Chim. Phys.,* 1883, [5], **29**, 445 ; Hedvall, *Zeitsch. anorg. Chem.,* 1916, **98**, 57.

in solution.[1]   Barium silicate is formed on the walls of glass vessels containing barium hydroxide solution.[2]

The anhydrous metasilicate forms small crystals showing a weak double refraction.   The density is 4·435 and melting-point 1604° C.[3] The heat of formation from barium oxide and silica is 26·3 Cal.[4]

The metasilicate is not isomorphous with calcium or strontium metasilicates.   With a-calcium metasilicate it forms a double compound, $2CaO.BaO.3SiO_2$.[5]

By treatment of hydrated silicic acid, or powdered quartz, with barium hydroxide solution, or by boiling barium metasilicate with water for some time, a number of hydrated acid silicates may be obtained.[6] Crystals of barium disilicate, $BaSi_2O_5$, have been observed to separate in optical glass in the form of hexagonal plates.[7]

A compound, $2BaO.3SiO_2$, which forms a complete series of solid solutions with the disilicates is also known.[5]

The use of barium silicate as a constituent of glass has already been mentioned.[8]   Its employment was first suggested by Döbereiner in 1829, and its effect upon the properties of the glass is much the same as that of lead.   It gives a higher refractive index and greater brilliancy than lime alone, and it has the additional advantage over lead of being unaffected by the products of combustion in the furnace.[9]

With barium aluminate a cement may be formed of composition $2(SiO_2.2BaO).Al_2O_3.2BaO$.   It sets hard with water, but, after some time, it splits, becomes soft, and deposits crystals of barium hydroxide.[10]

Barium Fluosilicate, $BaSiF_6$, is obtained by precipitation of a barium salt with hydrofluosilicic acid.[11]   It forms microscopic needles of density 4·28 at 21° C.[12]   It is not very soluble in water, one part dissolving in 3731 parts of water at 17·5° C., and in 1175 parts at 100° C. It is practically insoluble in alcohol, but dissolves with decomposition in dilute hydrochloric acid.   On calcination, silicon fluoride is given off and barium fluoride remains.[12]

BARIUM AND TIN.

Barium Stannate, $2BaO.SnO_2.10H_2O$, is obtained in the form of brilliant pearly leaflets by the action of a solution of potassium stannate on a saturated solution of a barium salt or of barium hydroxide.[13]   Like the calcium and strontium compounds, it is insoluble in water but dis-

[1] Le Chatelier, *Bull. Soc. chim.*, 1884, [2], **42**, 82 ; *Compt. rend.*, 1881, **92**, 931 ; *La Silice et les Silicates* (Hermann et Fils, Paris), 1914, p. 410 ; see also Wahl, *J. Chem. Soc.*, 1902, **82**, Abs. ii, 501 ; van Bemmelen, *Zeitsch. anorg. Chem.*, 1903, **36**, 393 ; Jaeger, *ibid.*, 400.

[2] Pisani, *Compt. rend.*, 1876, **83**, 1056.

[3] Jäger and van Klooster, *Sprechsaal*, 1919, **52**, 256, see *J. Soc. Glass Tech.*, 1919, **3**, 234A.

[4] Le Chatelier, *La Silice et les Silicates* (Hermann et Fils), 1914, p. 52.

[5] Eskola, *Amer. J. Sci.*, 1922, [5], **4**, 331.

[6] Jordis and Kanter, *Zeitsch. anorg. Chem.*, 1903, **35**, 148, 336 ; 1905, **43**, 314.

[7] Bowen, *J. Wash. Acad. Sci.*, 1918, **8**, 265, see *J. Chem. Soc.*, 1918, **114**, Abs. ii, 198.

[8] See Calcium, under Glass.

[9] Silverman, *J. Soc Chem. Ind.*, 1915, **34**, 399.

[10] Zulkowski, *ibid.*, 1901, **20**, 990.

[11] Gay-Lussac and Thénard, *Ann. Chim.*, 1809, [1], **69**, 214.

[12] Stolba, *J. prakt. Chem.*, 1865, [1], **96**, 22.

[13] Ditte, *Compt. rend.*, 1883, **96**, 701.

solves in cold hydrochloric or nitric acid, forming a clear solution which gelatinises on heating.

Both a chlorostannite, $BaSnCl_4.4H_2O$,[1] and a chlorostannate, $BaSnCl_6.5H_2O$,[2] are known, and also a fluorstannate, $BaSnF_6.3H_2O$,[3] and a thiostannate, $BaSnS_3.8H_2O$.[4]

BARIUM AND LEAD.

Barium Orthoplumbate, Ba_2PbO_4, is obtained as a black compound by gently heating lead oxide with barium oxide or barium carbonate in air at bright red heat. It is insoluble in water, but is decomposed by long contact with it. With hydrochloric acid it gives chlorine, and with other acids lead peroxide.[5]

BARIUM AND TITANIUM.

Barium Titanate, $BaTiO_3$, has been obtained in an amorphous form by heating barium fluoroxytitanate.[6] By heating together titanium oxide, barium carbonate, and barium chloride, brilliant, strongly refracting, yellow, cubic crystals, of density 5·91 and composition $2BaO.3TiO_2$, are obtained.[7]

A barium fluortitanate, $BaTiF_6.\frac{1}{2}H_2O$,[3] is known, and also a natural silicotitanate, *benitoite*, $BaSi_3TiO_9$, in beautiful, hexagonal, sapphire-blue prisms.[8]

Barium Pertitanate, or Barium Peroxide Pertitanate, BaO_2. $TiO_3.5H_2O$, is obtained by the action of sodium pertitanate, $Na_2O_2.TiO_3$, on barium chloride. It forms a voluminous yellow precipitate which may be dried over sulphuric acid. Hydrogen peroxide is liberated from it by dilute sulphuric acid, indicating the presence of the barium peroxide structure, and with hydrochloric acid chlorine is evolved.[9]

Barium Fluoroxytitanate, $BaTiO_2F_4$, or $BaF_2.TiO_2F_2$, is prepared as a flocculent precipitate, soluble in acids, by treating a soluble barium salt with ammonium fluoroxytitanate.[10] A yellow substance of composition $3BaF_2.2TiO_2F_2$ is probably also formed at the same time.

BARIUM AND ZIRCONIUM.

Barium Zirconate, $BaZrO_3$, is obtained by fusing zirconium oxide with barium hydroxide. After treatment with water and dilute acetic acid a fine greyish-white powder, easily soluble in hydrochloric acid, is obtained.[11] Barium chloride may be used instead of the hydroxide.[12]

[1] Poggiale, *Compt. rend.*, 1845, 20, 1183.
[2] Lewy, *Ann. Chim. Phys.*, 1846, [3], 16, 306.
[3] Emich, *Monatsh.*, 1904, 25, 907.
[4] Ditte, *Compt. rend.*, 1882, 95, 641.
[5] Kassner, *Arch. Pharm.*, 1890, 8, 109.
[6] Piccini, *Gazzetta*, 1887, 17, 479.
[7] Bourgeois, *Compt. rend.*, 1886, 103, 141; *Bull. Soc. chim.*, 1886, [2], 46, 262
[8] Smolensky, *Zeitsch. anorg. Chem.*, 1912, 73, 303.
[9] Melikoff and Pissarjewsky, *Ber.*, 1898, 31, 953.
[10] Piccini, *loc. cit*; *Jahresber.*, 1885, 549
[11] Venable and Clarke, *J. Amer. Chem. Soc.*, 1896, 18, 434.
[12] Ouvrard, *Compt. rend.*, 1891, 113, 80.

By mixing solutions of barium chloride and potassium fluorzirconate a precipitate of composition $3BaF_2.2ZrF_4.2H_2O$ is obtained, but this may be either a compound or a mixture.[1]

BARIUM AND BORON.

Barium Boride, BaB_6, is obtained by heating together, in the electric furnace, barium borate, aluminium, and carbon. It is more readily prepared than strontium and calcium borides, the yields being larger and of greater purity.[2] Its density is 4·36 at 15° C., and in hardness it lies between diamond and ruby or quartz. Its chemical properties are similar to those of calcium and strontium borides.[2] By the action of calcium on barium borate a mixture of the two borides is always obtained.[3]

Barium Borates.—Guertler studied the freezing-point curves of mixtures of barium oxide and boric anhydride and came to the conclusion that the following chemical individuals exist : the orthoborate, $3BaO.B_2O_3$, the pyroborate, $2BaO.B_2O_3$, in a crystalline marble-like mass, the metaborate, $BaO.B_2O_3$, crystallising in flat prisms, and the biborate, $BaO.2B_2O_3$, which does not readily crystallise.[4]

Precipitates of varying composition are obtained by mixing solutions of borax and a soluble barium salt, or by the interaction of barium hydroxide with boric anhydride.[5] They are soluble in solutions of ammonia salts, and the action of carbon dioxide has also been studied.[6]

The system $BaO : B_2O_3 : H_2O$ has been investigated by Sborgi, who confirmed the existence of the following compounds : $BaO.B_2O_3.4H_2O$, $2BaO.3B_2O_3.6H_2O$, and $BaO.3B_2O_3.7H_2O$.[7]

Barium Fluorborate, $BaBF_5.2H_2O$, is obtained by evaporation of a solution of barium carbonate in excess of fluorboric acid. It forms quadratic prisms soluble in water. The water of crystallisation is lost at 40° C.[8]

Barium Perborate, $Ba(BO_3)_2.7H_2O$, is formed as a white flocculent precipitate by the action of sodium perborate on barium chloride at 0° C. It decomposes hydrochloric acid with the evolution of chlorine, and reacts with sulphuric acid producing barium sulphate and hydrogen peroxide.[9]

By the action of boric acid on hydrated barium peroxide a compound, $BaB_2O_5.3H_2O$, is obtained.[10]

[1] Marignac, *Ann. Chim. Phys.*, 1860, [3], 60, 279.

[2] Moissan and Williams, *Compt. rend.*, 1897, 125, 629 ; Moissan, *Electric Furnace,* English translation (Williams & Norgate), 1908.

[3] Wedekind, *Ber.*, 1913, 46, 1885.

[4] Guertler, *Zeitsch. anorg. Chem.*, 1904, 40, 337 ; see also Benedikt, *Ber.*, 1874, 7, 703 ; Ouvrard, *Compt. rend.*, 1901, 132, 257 ; Ditte, *ibid.*, 1873, 77, 783, 892 ; Bloxam, *J. Chem. Soc.*, 1862, 14, 147.

[5] Rose, *Pogg. Annalen*, 1852, 87, 1 ; Ditte, *Ann. Chim. Phys.*, 1883, [5], 30, 248 ; Laurent, *Annalen*, 1850, 76, 263.

[6] Morse and Horn, *Amer. Chem. J.*, 1900, 24, 105.

[7] Sborgi, *Atti R. Accad. Lincei*, 1914, [5], 23, 1, 530, 717, 854 ; see also Atterberg, *Bull. Soc. chim.*, 1874, [2], 22, 350 ; *Zeitsch. anorg. Chem.*, 1906, 48, 372 ; Levi and Castellani, *Atti R. Accad. Lincei*, 1908, [5], 17, ii, 613.

[8] Berzelius, *Pogg. Annalen*, 1824, 2, 123.

[9] Melikoff and Pissarjewsky, *Ber.*, 1898, 31, 678, 953.

[10] Etard, *Compt. rend.*, 1880, 91, 931.

BARIUM AND ALUMINIUM.

Barium Aluminates.—Freshly precipitated aluminium hydroxide is dissolved by barium hydroxide solution with the formation of barium aluminates. Metallic aluminium is also attacked by barium hydroxide solution. The following compounds have been described : $Al_2O_3.BaO.6H_2O$, or $5H_2O$, $Al_2O_3.2BaO.5H_2O$, and $Al_2O_3.3BaO.11H_2O$. Lower hydrates may be obtained by heating.[1] Halogen compounds are also known, $Al_2O_3.BaO.3BaCl_2.6H_2O$, $Al_2O_3.BaO.BaCl_2.11H_2O$, $Al_2O_3.BaO.BaBr_2.11H_2O$, and $Al_2O_3.BaO.BaI_2.11H_2O$.[2]

BARIUM AND THE IRON GROUP.

Barium Ferrite, $BaO.Fe_2O_3$, is obtained in small dark brown crystals by heating barium ferrate with a mixture of barium oxide and barium chloride at 800°–1300° C. Oxygen is evolved. The higher the temperature employed the larger the amount of oxide necessary.[3]

Barium Ferrate, $BaO.FeO_3.H_2O$, may be obtained by precipitating potassium ferrate with barium nitrate,[4] or chloride,[5] or by acting on barium chromate with sodium ferrate. It forms a purplered powder, extremely insoluble in water,[6] and is the most stable of the ferrates.[4] When heated it decomposes into oxygen, ferric oxide, and barium oxide.[3] It may also be formed by the action of strontium ferrate on barium sulphate, oxalate, or carbonate.[7] It is not affected by dilute sulphuric acid in the cold, but is completely decomposed by boiling sulphuric acid. With dilute nitric or hydrochloric acid there is almost instantaneous decomposition with formation of salts of iron and of barium, and, in the case of the hydrochloric acid, with evolution of chlorine also. Barium ferrate dissolves also in organic acids.[4,8]

Barium Cobaltite.—When a mixture of cobalt sesquioxide, barium oxide, and barium chloride or bromide is heated to redness, or about 800° C., and the product washed with hot water and then with acetic acid, brilliant black hexagonal plates of the composition $BaO.2CoO_2$ are formed. When this compound is treated with concentrated hydrochloric acid, chlorine is evolved. At higher temperatures, 1000°–1100° C., a monocobaltite, in large iridescent black prisms, is formed.[9]

Barium Dinickelite, $BaO.2NiO_2$, is obtained by heating an intimate mixture of barium oxide and nickel sesquioxide in the electric furnace. It forms a greenish-brown crystalline powder of density 4·8 at 20° C., and hardness 4 on Mohs' scale. It is decomposed by water, and is readily attacked by anhydrous hydrochloric and hydrofluoric acid, chlorine, bromine, and sulphur, but not by oxygen. Neutral oxidising agents, for example potassium nitrate, are without action upon it.[10]

[1] Beckmann, *Ber.*, 1881, **14**, 2151; *J prakt. Chem.*, 1882, [2], **26**, 385; Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 311.

[2] Beckmann, *Ber.*, 1881, **14**, 2151; *J. prakt. Chem.*, 1882, [2], **26**, 474.

[3] Rousseau and Bernheim, *Compt. rend.*, 1888, **106**, 1726.

[1] Frémy, *Ann. Chim. Phys.*, 1844, [3], **12**, 373.

[5] Bloxam, *Chem. News*, 1886, **54**, 43.

[6] Rosell, *J. Amer. Chem. Soc.*, 1895, **17**, 760.

[7] Eidmann and Moeser, *Ber.*, 1903, **36**, 2290.

[8] Baschieri, *Gazzetta*, 1906, **36**, ii, 282.

[9] Rousseau, *Compt. rend.*, 1889, **109**, 64 Dufau, *Ann. Chim. Phys.*, 1897, [7], **12**, 257.

[10] Dufau, *loc. cit.*

BARIUM AND PLATINUM.

Barium Platinate, $3BaO.PtO_2$, is formed when barium oxide is heated with the chloride or bromide in an open platinum crucible for several hours at 1100° C. It is more readily obtained by preparing first the amorphous platinate by heating platinic chloride with barium oxide and then fusing with barium chloride or bromide to obtain the crystalline product. It forms hexagonal prisms insoluble in acetic but soluble in hydrochloric acid. When very strongly heated it decomposes with the separation of platinum.[1]

DETECTION AND ESTIMATION OF BARIUM.

Dry Tests.—Volatile barium salts give a yellowish-green coloration to the non-luminous flame. Like the other alkaline earths, barium has a characteristic spectrum. The most prominent line to be observed by the eye has a wave-length 5535·5 Å.[2] By de Gramont's photographic method the lines 4934 and 4554 Å are the most distinctive, but the line 3891·8 is also a sensitive ray.[2]

When heated with sodium carbonate on charcoal the oxide is not formed, so that a brightly luminous mass is not obtained, and this affords a distinction from the other alkaline earths.

Wet Tests.—By the spectroscopic method of Riesenfeld and Pfutzer already mentioned under calcium and strontium, barium in a solution of concentration 0·0006 mgm. per c.c. may be detected by the lines 6497, 4934, and 4554 Å. The lines 6142 and 5536 Å also show faintly.[3]

The chief method of separating barium from admixture with the other alkaline earths, namely by precipitation of the chromate in acetic acid solution, has already been incidentally mentioned under calcium and strontium. Other confirmatory tests may be applied—for example, the precipitation of the sulphate by strontium sulphate, or of the chromate by strontium chromate, and the precipitation of the fluosilicate by hydrofluosilicic acid in aqueous or alcoholic solution, or by aniline fluosilicate.[4] Precipitation by alcoholic thiosulphate has also been suggested.[5]

Similar microchemical tests to those employed in the case of calcium or strontium may be applied.[6]

Quantitative Estimation of Barium.—The determination of barium by precipitation of the sulphate is the method in most general use, and, therefore, the one which has received the most careful study. Its great drawback, in addition to the effect of the medium on the solubility of the precipitate, which must be considered in all precipitation methods, is the pronounced tendency of barium sulphate to occlude

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[1] Rousseau, *Compt. rend.*, 1889, **109**, 144.

[2] de Gramont, *ibid.*, 1920, **171**, 1106; see also Riesenfeld and Wohlers, who give the lines 5242 and 5137 Å as the most convenient for detection, *Ber.*, 1906, **39**, 2628.

[3] Riesenfeld and Pfutzer, *Ber.*, 1913, **46**, 3140.

[4] Caron and Raquet, *Bull. Soc. chim.*, 1908, [4], **3**, 483; Lutz, *Zeitsch. anal. Chem.*, 1921, **60**, 209; Lutz compares the values of the different precipitants for analytical purposes.

[5] Polonovski, *Bull. Soc. chim.*, 1922, [4], **31**, 806.

[6] Denigès, *Compt. rend.*, 1920, **170**, 996; **171**, 633; Schoorl, *Zeitsch. anal. Chem.*, 1909, **48**, 401; see also Bolland, *Compt. rend.*, 1920, **171**, 955.

foreign salts, whether by chemical combination or physical adsorption. There is a large literature on the subject,[1] and some of the results may be briefly summarised.

Excess of barium chloride should be avoided. Alkali and ammonium nitrates and sulphates are occluded to a greater extent than chlorides. Salts of heavy metals and aluminium are carried down, and also calcium sulphate, but the latter at the same time apparently prevents the occlusion of potassium, sodium, magnesium, iron, or cobalt compounds. Adsorption may be diminished by rapid stirring.[2]

Alkali and ammonium salts, ferric chloride, free chlorine and bromine, hydrochloric, nitric, and metaphosphoric acids increase the solubility. A slight loss may also take place on ignition under certain circumstances. Arbitrary corrections to be added or subtracted from the calculated result, according to the procedure employed, have been suggested, but it is probably preferable to calibrate the method used by pure sodium sulphate or potassium sulphate in strongly acid solution.[3] It has also been stated that, owing to partial compensation of opposing errors, a very good uncorrected determination may be made by precipitating rapidly.[4]

The general behaviour of the barium sulphate precipitate, for example, the dependence of the amount of foreign substance taken up on the concentration of the solution and on the fineness of the precipitate, seems to indicate that the phenomenon is one of adsorption at the surface.[3]

The precipitation of barium chromate is also employed as a method of estimation. Ammonium dichromate solution in the presence of ammonium acetate,[5] or of acetic acid and ammonium chromate,[6] may be used. In the presence of strontium a solid solution of strontium chromate in barium chromate is apparently formed,[7] and two precipitations are necessary to give a satisfactory result.[8]

The precipitation of the chloride by hydrochloric acid and ether might be employed for the estimation of barium in the presence of strontium chloride,[9] or precipitation by a mixture of acetone and acetyl

[1] The following are references to the more recent literature on the subject : Fresenius, *Zeitsch. anal. Chem.*, 1891, 30, 452, 583 ; Kuster and Thiel, *Zeitsch. anorg. Chem.*, 1899, 19, 97 ; 21, 73 ; 1900, 22, 424 ; 25, 319 ; Lunge, *ibid.*, 1899, 19, 454 ; 21, 194 ; Richards, *ibid.*, 1900, 23, 383 ; Patten, *J. Amer. Chem. Soc.*, 1903, 25, 186 ; Hulett and Duschak, *Zeitsch. anorg. Chem.*, 1904, 40, 196 ; Korte, *Trans. Chem. Soc.*, 1905, 87, 1503 ; Skrabal and Artmann, *Zeitsch. anal. Chem.*, 1906, 45, 584 ; Frion, *Compt. rend.*, 1908, 146, 925 ; van't Kruijs, *Chem. Weekblad*, 1909, 6, 735 ; Creighton, *Zeitsch. anorg. Chem.*, 1909, 63, 53 ; Allen and Johnston, *J. Amer. Chem. Soc.*, 1910, 32, 588 ; Johnston and Adams, *ibid.*, 1911, 33, 829 ; Gooch and Hill, *Amer. J. Sci.*, 1913, [4], 35, 311 ; Osborne, *J. Physical Chem.*, 1913, 17, 629 ; Kling and Lassieur, *Compt. rend.*, 1914, 158, 487 ; Karaoglanow, *Zeitsch. anal. Chem.*, 1917, 56, 417, 487 ; 1918, 57, 113 ; *Zeitsch. angew. Chem.*, 1918, 31, 160 ; Winkler, *ibid.*, 1917, 30, 251, 259, 301 ; 1920, 33, 59, 287, 299 ; Weiser and Sherrick, *J. Physical Chem.*, 1919, 23, 205 ; Teodossiu, *J. Chem. Soc.*, 1921, 120, Abs. ii, 521 ; Balareff, *Zeitsch. anorg. Chem.*, 1922, 123, 69.

[2] Dutoit and Grobet, *J. Chim. phys.*, 1922, 19, 328.

[3] Johnston and Adams, *loc. cit.*

[4] Allen and Johnston, *loc. cit.*

[5] Fresenius, *Zeitsch. anal. Chem.*, 1891, 30, 18 ; Skrabal and Neustadtl, *ibid.*, 1905, 44, 742 ; Kahan, *Analyst*, 1908, 33, 12.

[6] van den Bos, *Chem. Weekblad*, 1911, 8, 5 ; see also Robin, *Compt. rend.*, 1903, 37, 258.

[7] Duschak, *J. Amer. Chem. Soc.*, 1908, 30, 1827.

[8] Fresenius, *Zeitsch. anal. Chem.*, 1890, 29, 413.

[9] Gooch and Soderman, *Amer. J. Sci.*, 1918, [4], 46, 538.

chloride in the presence of calcium and magnesium.[1]   Precipitation of barium as the fluosilicate may also be used in the presence of strontium[2] and calcium.[3]

Precipitation by chromate is employed in the volumetric estimation of barium, the latter being precipitated by a known amount of chromate and the excess chromate being titrated by potassium iodide and thiosulphate.[4]   Barium may also be precipitated as oxalate and estimated volumetrically.[5]   Another volumetric method depends on the precipitation of the iodate, treatment of the latter with hydrochloric acid and potassium iodide, and titration of the liberated iodine.   Strontium and calcium must not be present.[6]   For an approximate volumetric estimation, precipitation by alcoholic thiosulphate might be used.[7]

Electrical Conductivity Methods may be employed as in the case of calcium and strontium.[8]   The sulphate, chromate, fluosilicate, and carbonate are suitable for precipitation.   For estimating calcium, strontium, and barium in a mixture by this method the following procedure may be adopted.   The solution is divided into three parts.   To the first is added two volumes of alcohol, and the solution is titrated with lithium sulphate.   This gives the total titration for barium, strontium, and calcium.   After addition of one volume of alcohol the second portion is titrated with lithium chromate, giving barium and strontium ; and the third portion, also with the addition of one volume of alcohol, is titrated with cupric fluosilicate, giving barium.   From these data the percentages of the three may be calculated.

Electrolytic Methods of separation and estimation have also been suggested.[9]

[1] Gooch and Boynton, *Amer J. Sci.*, 1911, [4], **31**, 212.
[2] Fresenius, *Zeitsch. anal. Chem.*, 1890, **29**, 149.
[3] Fresenius, *ibid.*, 1891, **30**, 18.
[4] van den Bos, *loc. cit.* ; Kolthoff, *Pharm Weekblad.* 1920, **57**, 972 ; Selvatici, *Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 862 ; Waddell, *Analyst*, 1918, **43**, 287.
[5] Peters, *Amer. J. Sci.*, 1901, [4], **12**, 216.
[6] Hill and Zink, *J. Amer. Chem. Soc.*, 1909, **31**, 43.
[7] Polonovski, *Bull. Soc. chim.*, 1922, [4], **31**, 810.
[8] Dutoit, *J. Chim. phys.*, 1910, 8, 12 ; and with Mojoiu, *ibid.*, 27.
[9] See Estimation of Calcium.

CHAPTER V.

RADIUM AND ITS COMPOUNDS.

RADIUM.

Symbol, Ra.   Atomic Weight, $225 \cdot 95 (O = 16)$.

Occurrence.—Radium is found in all minerals containing uranium, and in no others, with one exception. Danne found at Issy l'Evêque a sample of *pyromorphite* which contained radium but no uranium.[1] This proved to be all in the surface layers and had no doubt been precipitated by water which had passed through neighbouring uranium deposits.[2]

The richest uranium minerals, and, consequently, as will be seen later, the richest radium minerals, are : *pitchblende* or *uraninite*, which is chiefly the uranium oxide, U_3O_8, and is found in Joachimsthal, Norway, Cornwall, the United States, and East Africa ; *carnotite*, a double vanadate of uranium and potassium, $K_2(UO_2)_2(VO_4)_2.8H_2O$,[3] found in the United States, chiefly Colorado and Utah, in Russia, especially Asiatic Russia, and also in South Australia ; *autunite*, or *uranium mica*, a double phosphate of calcium and uranium, $Ca(UO_2)_2(PO_4)_2.8H_2O$, principally from Portugal ; and *chalcolite*, a double phosphate of uranium and copper, $Cu(UO_2)_2(PO_4)_2.8H_2O$, from Central Europe, Portugal, and Cornwall. With pitchblende may also be included *cleveite*, a hydroxide of uranium, lead, thorium, yttrium, and other rare earths, and *bröggerite*, resembling pitchblende but containing thorium, from Norway.

There are numerous other minerals of less importance, *gummite*, a decomposition product of uraninite $(Pb,Ca,Ba)U_3SiO_{12}.6H_2O$, *blomstrandite*, uranium tantalocolumbate, *fergusonite*, orthocolumbate and tantalate of rare earths, *samarskite*, paracolumbate and paratantalate of uranium, thorium, and rare earths, *uranocircite*, $Ba(UO_2)_2(PO_4)_2.$ $8H_2O$, *uranocalcite*, hydrated sulphate of calcium, uranium, iron, and copper, *uranophane*, $CaO.2UO_3.2SiO_2.6H_2O$,[4] and so on.[5]

The radium found in the richest of these minerals does not greatly exceed 2×10^{-7} gram per gram, but in far more minute quantities, of

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[1] Danne, *Compt. rend.*, 1905, **140**, 241.

[2] McCoy, *J. Amer. Chem. Soc.*, 1907, **29**, 1702.   According to Bamberger and Weissenberger, *Monatsh.*, 1915, **36**, 169, pyromorphite is homogeneous in radium.

[3] Browning, *Introduction to the Rarer Elements* (Wiley, New York ; Chapman & Hall, London), 1917.   Friedel and Cumenge, *Compt. rend.*, 1899, **128**, 532, gave the formula $K_2(UO_2)_2(VO_4)_2.3H_2O$, but there appears to be some doubt as to whether carnotite is a true mineral or simply a mixture (see Hillebrand and Ransome, *Amer. J. Sci.*, 1900, [4], **10**, 120).   Wherry gives the formula $(Ca,K_2)(UO_2)_2(VO_4)_2.XH_2O$, where X is approximately 8, *Amer. J. Sci.*, 1912, [4], **33**, 574.

[4] Watson, *Amer. J. Sci.*, 1902, [4], **13**, 464.

[5] See Szilard, *Le Radium*, 1909, **6**, 233, who gives a list of radioactive minerals, and a map showing their distribution.

the order of 10^{-12} gram per gram, it is found in almost all rocks, more being found in primary than in sedimentary rocks owing to the washing out of some of the radium in the formation of the latter.[1]

In insignificant traces it has been found in stone meteorites,[2] but not in metallic ones,[3] and there are rather doubtful spectroscopic indications of its presence in the sun [4] and in new stars.[5]

Radium, or its products of radioactive disintegration, has also been detected in the water and sediment of many mineral springs,[6] in seawater,[7] and in the atmosphere.[8]

History.—The history of radium may, to a large extent, be regarded as the history of radioactivity, because, although the phenomena connected with the property of radioactivity were first observed by Becquerel in uranium,[9] it was the discovery of radium which focussed the attention of both the scientific and the lay world on the subject; and it is radium which has always been regarded as the typical radioactive element.

During an investigation of the ionising power [10] of uranium minerals Mme. Curie observed that natural uranium minerals had a greater activity than uranium salts of the same composition prepared artificially, and she therefore carried out a chemical separation of pitchblende from Joachimsthal, given by the Austrian Government, with a view to determining to what constituent the increased activity was to be ascribed. An extraordinarily active substance, in minute quantity,

[1] Strutt, *Jahrb. Radioakt. Elektron.*, 1904, **1**, 12; *Proc. Roy. Soc.*, 1906, **77A**, 472, 1910, **84A**, 377; *Le Radium*, 1906, **3**, 161; Eve and McIntosh, *Phil. Mag.*, 1907, [6], **14**, 231; Waters, *ibid.*, 1910, [6], **19**, 903. Fair and Florance, *ibid.*, 1909, [6], **18**, 812; Gockel, *Jahrb. Radioakt. Elektron.*, 1910, **7**, 487; Joly, *Phil. Mag.*, 1909, **18**, 577; 1911, [6], **22**, 134; 1912, [6], **24**, 694; Fletcher, *ibid.*. 1910, [6], **20**, 36; 1912, [6], **23**, 279; Buchner, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 359; *Jahrb. Radioakt. Elektron.*, 1913, **10**, 516; Smeeth and Watson, *Phil. Mag.*, 1918, [6], **35**, 206; Holmes, *The Age of the Earth* (Harper), 1913, p 131.

[2] Quirke and Finkelstein, *Amer. J. Sci.*, 1917, [4], **44**, 237.

[3] Strutt, *Le Radium*, 1906, **3**, 161; *Proc. Roy. Soc.*, 1906, **77A**, 472.

[4] Sana, *Phil. Mag.*, 1920, [6], **40**, 809; Dyson, *Astr. Nachr.*, 1912, **192**, July, No. 4589, see *Sci. Abs.*, 1912, [A], **15**, 518; Vegard, *Phil. Mag.*, 1912, [6], **23**, 211, from consideration of the aurora.

[5] Giebeler, *Astr. Nachr.*, 1912, **191**, June, No. 4582, see *Sci. Abs.*, 1912, [A], **15**, 518.

[6] Strutt, *Nature*, 1904, **69**, 474; *Jahrb. Radioakt. Elektron.*, 1905, **2**, 12; Laborde, *Le Radium*, 1904, **1**, 1; Gockel, *Physikal. Zeitsch.*, 1904, **5**, 594; Boltwood, *Amer. J. Sci.*, 1904, [4], **18**, 378; Henrich, *Zeitsch. angew. Chem.*, 1904, **17**, 175; *Zeitsch. anorg. Chem.*, 1909, **65**, 117; Blanc, *Phil. Mag.*, 1905, [6], **9**, 148; Borne, *Jahrb. Radioakt. Elektron.*, 1905, **2**, 77, 142; Elster and Geitel, *Physikal. Zeitsch.*, 1905, **6**, 67; Mache and Meyer, *ibid.*, 1905, **6**, 692; Koch, *ibid.*, 1906, **7**, 806; Schmidt, *ibid.*, 1907, **8**, 1; Curie and Laborde, *Compt. rend.*, 1906, **142**, 1462; Sahlbom and Hinrichsen, *Ber.*, 1906, **39**, 2607; Ramsay, *Chem. News*, 1912, **105**, 133; Kruse, *Jahrb. Radioakt. Elektron.*, 1917, **14**, 352; Lester, *Amer. J. Sci.*, 1918, [4], **46**, 621.

[7] Joly, *Phil. Mag.*, 1908, [6], **15**, 385; 1909, **18**, 396; Eve, *Nature*, 1908, **78**, 604; *Phil. Mag.*, 1909, [6], **18**, 102; Satterly, *Proc. Camb. Phil. Soc.*, 1911, **16**, 360; Knoche, *Physikal. Zeitsch.*, 1912, **13**, 112, 152.

[8] Elster and Geitel, *Physikal. Zeitsch.*, 1902, **3**, 574; Gockel, *ibid.*, 1904, **5**, 591; 1908, **9**, 304; Eve, *Phil. Mag.*, 1905, [6], **10**, 98; 1906, **12**, 189; 1907, **13**, 248; **14**, 724; 1908, **16**, 622; Dadourian, *Amer. J. Sci.*, 1905, [4], **19**, 16; 1908, **25**, 335; Mache and Rimmer, *Physikal. Zeitsch.*, 1906, **7**, 617; Blanc, *Phil. Mag.*, 1907, [6], **13**, 378; *Jahrb. Radioakt. Elektron.*, 1909, **6**, 502; Henrich, *Zeitsch. Elektrochem.*, 1907, **13**, 393; Satterly, *Phil. Mag.*, 1908, [6], **16**, 584; 1910, [6], **20**, 1; Wilson, *ibid.*, 1909, **17**, 321; Kinoshita, Nishikawa, and Ono, *ibid.*, 1911, [6], **22**, 821; Kohlrausch, *Physikal. Zeitsch.*, 1912, **13**, 1193; Harvey, *Phys. Review*, 1912, [1], **35**, 120; Allen, *ibid.*, 1916, [2], **7**, 133; Hess and Schmidt, *Physikal. Zeitsch.*, 1918, **19**, 109; Bongards, *ibid.*, 1920, **21**, 141.

[9] Becquerel, *Compt. rend.*, 1896, **122**, 420, 501, 559, 689, 762, 1086.

[10] See later the section on Radioactive Phenomena.

was found to be precipitated with the alkaline earths, and the name radium was given to it.[1]   Another radioactive substance, polonium, which was shown later to be derived from radium, was also found, being precipitated along with bismuth.[2]

Radium was at first only separated in the form of its salts, the chloride and the bromide, but in 1910 it was obtained in the metallic state by methods which are valid also for the separation of the other metals of the alkaline earth group.

Preparation of Radium Salts.—*Extraction of Radium Salts from Uranium Ores.*—Pitchblende was at first the most important source of radium, and the separation was carried out in France, Germany, and Austria.   The Joachimsthal deposits, however, are reported to be almost worked out, and in recent years America has begun to treat carnotite ores on an extensive scale for the production of radium.

Various modes of treatment are employed.[3]   The original method [4] was to roast the ore with sodium carbonate, wash with warm water, and then with dilute sulphuric acid, thus obtaining an insoluble residue containing both the radium and the polonium and leaving the uranium in solution.   By boiling with sodium carbonate solution, the sulphate residue was then converted into carbonates, which could be attacked by hydrochloric acid and submitted to an analytical separation.   The radium was ultimately obtained as chloride along with the barium.

By the Ulzer-Sommer process [5] the ore is first treated with concentrated sulphuric acid for some weeks at normal temperature, or for a few hours at boiling temperature, or fused with acid sulphates.   The residue is well washed and fused with sodium hydroxide or carbonate, or boiled under pressure with a concentrated solution of these.   After further washing, the residue is boiled with dilute sulphuric acid, the radium and barium thus being obtained as sulphates.

For American pitchblende ores, especially where the uraninite is intimately associated with iron pyrites, a chlorination process has been suggested.[6]

For the treatment of carnotite ores the transformation of the mineral into partly soluble vanadates and uranates by the action of sodium hydroxide and carbonate has been proposed.[7]   The residue, after washing, may be extracted with dilute hydrochloric acid, forming radium, vanadyl, and uranyl chlorides.   Sodium carbonate precipitates radium carbonate and part of the sodium vanadate.   By the addition of sulphuric acid, radium sulphate is formed and vanadyl sulphate goes into solution.

Ebler and Bender suggested the reduction of sulphates to sulphide

[1] M. and Mme. Curie, and Bémont, *Compt. rend.*, 1898, **127**, 1215.

[2] M. and Mme. Curie, *ibid.*, 1898, **127**, 175 ; see also Mme. Curie, *Ann. Chim. Phys.*, 1903, [7], **30**, 99, 145, 289 ; *Thèse présentée à la Faculté des Sciences de Paris*, 1903, English translation reprinted from *Chem. News*, 1904 ; *Traité de Radioactivité* (Gauthier-Villars, Paris), 1910, vol. i, p. 148 ; Rutherford, *Radioactive Substances and their Radiations* (Cambridge University Press), 1913.

[3] Martin, *Industrial Chemistry, Inorganic*, vol. ii. (Crosby Lockwood & Son), 1917, article by Russell on *Industry of Radioactive Substances*, p. 383 ; Ebler and Bender, *Zeitsch. angew. Chem.*, 1915, **28**, 25 ; Haitinger and Ulrich, *Sitzungsber. K. Akad. Wiss. Wien*, 1908, **117**, 619 ; *Monatsh.*, 1908, **29**, 485.

[4] Curie, *loc. cit.*

[5] English Patent, 19820 (Aug. 30, 1909), see *J. Soc. Chem. Ind.*, 1910, **29**, 1156.

[6] Cable and Schlundt, *Chem. News*, 1918, **117**, 244.

[7] Bleecker and Standard Chem. Co. of Pittsburg, U.S.A., U.S. Patent, 1068730 (1913) ; 1065581 (1913), see *J. Soc. Chem. Ind.*, 1913, **32**, 757, 871.

by calcium carbide or hydride, or preferably a mixture of the two.[1] The process is similar to the alumino-thermic method, the reaction being started with a fuse. The reaction product is cooled, powdered, rapidly dissolved in hot dilute hydrochloric acid, and hydrogen sulphide expelled by boiling. Lead sulphide and siliceous matter remain undissolved.

Soddy suggested the reduction of sulphates to sulphides by coal gas.[2]

For the treatment of carnotite ores, solution in boiling concentrated sulphuric acid, above 78 per cent., is apparently a promising method.[3] From a good ore at least 90 per cent. of the radium is said to be extracted, and from a poor one about 80 per cent. After the addition of a large volume of water the insoluble residue is subjected to differential sedimentation. The fine sediment contains 87 per cent. of the radium at 20–28 times the concentration in the ore. Fusion with sodium hydrogen sulphate may be employed instead.[4] A further concentration of the radium may be effected by solution in boiling concentrated sulphuric acid again and reprecipitation with water containing a trace of barium chloride, or by fusion with sodium carbonate and subsequent solution in hydrochloric acid.

Hot 38 per cent. nitric acid will dissolve most of the uranium and radium in carnotite. The solution may then be neutralised with caustic soda and the radium precipitated along with barium as the sulphate, reduced to sulphide by carbon in graphite crucibles at 800° C., and dissolved in hydrochloric acid.[5]

Carnotite may also be attacked by boiling concentrated sodium carbonate solution, the barium and radium being ultimately transformed into sulphates.[6]

For treatment of ores poor in radium Ebler and van Rhyn proposed heating to sintering temperature, 800°–1000° C., with sodium or calcium chloride and calcium carbonate for five to six hours in a muffle, and then powdering and extracting the cooled mass with dilute hydrochloric acid containing sulphuric acid and barium chloride. The crude sulphates then contain the radium in a much more concentrated form.[7]

In the treatment of the Australian Olary ores, which contain very little radium and consist mainly of silicotitanates of iron and the rare earths, the ore is first crushed, concentrated magnetically, and fused with sodium hydrogen sulphate. When crushed and agitated with water, coarse inactive particles are separated from a radioactive " slime." The latter is treated with sulphuric acid, washed, converted into carbonates, dissolved in hydrochloric acid, and reprecipitated as sulphates. These are fused with sodium carbonate in graphite pots and the product digested with hot water. After the metallic lead has been picked out the residue is heated with hydrochloric acid and the solution evaporated to dryness. By treating with hot dilute acid insoluble silica may be

[1] Ebler and Bender, *Zeitsch. anorg. Chem.*, 1913, **83**, 149; 1914, **88**, 255; *Zeitsch. angew. Chem.*, 1915, **28**, 35.

[2] Soddy, *The Chemistry of the Radio-Elements* (Longmans, Green & Co.), 1911, p. 45.

[3] Schlundt, *J. Physical Chem.*, 1916, **20**, 485; *Chem. News*, 1916, **114**, 50; Loomis and Schlundt, *J. Ind. Eng. Chem.*, 1916, **8**, 990.

[4] Schlundt, U.S. Patent, 1240607 (Sept. 18, 1917), see *J. Soc. Chem. Ind.*, 1917, **36**, 1137.

[5] Parsons, Moore, Lind, and Schaefer, *Chem. News*, 1916, **113**, 79.

[6] Plum, *J. Amer. Chem. Soc.*, 1915, **37**, 1797.

[7] Ebler and van Rhyn, *Zeitsch. angew. Chem.*, 1921, **34**, 477.

removed, and by saturation with hydrochloric acid gas radium and barium chloride may be precipitated.[1]

Purification of Radium Salts. — The method first employed by Mme. Curie for the separation of radium from the barium with which the crude salt is always associated was the fractional crystallisation of the chlorides, first from water and then from hydrochloric acid, the radium chloride being less soluble than the barium chloride. Giesel recommended the fractional crystallisation of the bromides.[2] Scholl has made a careful study of the two systems, $RaCl_2 : BaCl_2$ and $RaBr_2 : BaBr_2$, and concludes that fractional crystallisation of the bromides is the more efficient method.[3] The ratios of radium bromide to barium bromide separating under different conditions have also been determined. Apparently this is independent of the concentration of hydrobromic acid.[4]

Fractional separation of the hydroxides has also been proposed,[5] but this is said to be less efficient than the bromide method.[6]

Ebler and Bender have suggested the fractional adsorption of radium and barium salts by a colloid such as silica, or preferably colloidal hydrated manganese dioxide, and subsequent desorption by hydrochloric acid.[7]

Separation of Metallic Radium.—By the electrolysis of a methyl alcoholic solution of radium bromide with an amalgamated zinc cathode and a silver anode Coehn obtained, in 1904, a strongly radioactive product which was probably an amalgam of radium.[8]

Radium amalgam also appears to be formed when sodium amalgam is shaken with a solution of a radium salt.[9]

In 1910 Mme. Curie and Debierne isolated the metal by Guntz's method for barium. They prepared the amalgam electrolytically from about 0·1 grm. radium chloride and 10 grm. mercury and then distilled off the mercury from an iron boat in a quartz tube in an atmosphere of rigorously purified hydrogen.[10] Distillation was complete at 700° C.

Ebler stated that he had prepared metallic radium by the decomposition by heat of the azide, $Ra(N_3)_2$, which he found to be a very stable compound.[11] Herschfinkel, however, doubted the possibility of formation of radium azide, suggesting that it would be decomposed by the radiations from the radium,[12] although, according to Ebler, the corresponding barium salt is not decomposed by radium rays.

The Properties of Metallic Radium.—Since metallic radium can only be said with certainty to have been separated once, and that in very small quantity, no very precise account of its properties can be given.

It is a brilliant white metal of melting-point 700° C. It is much more volatile than barium, and the vapour attacks quartz energetically. In its behaviour towards chemical reagents it closely resembles metallic

[1] Radcliff, *J. Soc. Chem. Ind.*, 1914, **33**, 229.

[2] Giesel, *Ber.*, 1902, **35**, 3608.

[3] Scholl, *J. Amer. Chem. Soc.*, 1920, **42**, 889.

[4] Nierman, *J. Phys. Chem.*, 1920, **24**, 192.

[5] McCoy, U.S. Patent, 1103600, *J. Soc. Chem. Ind.*, 1914, **33**, 919.

[6] Strong, *J. Amer. Chem. Soc.*, 1921, **43**, 440 ; see also Francis, *J. Soc. Chem. Ind.*, 1922, **41**, 941.

[7] Ebler and Bender, *Zeitsch. anorg. Chem.*, 1913, **84**, 77 ; *Zeitsch. angew. Chem.*, 1915, **28**, 41 ; Ebler and Fellner, *Ber.*, 1911, **44**, 2332.

[8] Coehn, *Ber.*, 1904, **37**, 811 ; see also Berthier, *Le Radium*, 1904, **1**, 48.

[9] Marckwald, *Ber.*, 1904, **37**, 88.

[10] Curie and Debierne, *Compt. rend.*, 1910, **151**, 523.

[11] Ebler, *Ber.*, 1910, **43**, 2613.

[12] Herschfinkel, *Le Radium*, 1911, **8**, 299.

barium.[1] It is attacked by both the nitrogen and the oxygen of the air, forming the nitride and the oxide respectively. It is decomposed by cold water, the heat of reaction probably being about 90 Cal. per gram atom.[2] In contact with organic matter, paper for instance, the latter is charred.

Radium differs from the other alkaline earths in the luminescence which it has in common with its salts, and which is a consequence of the radioactive properties to be discussed later.

The following are the chief lines of the spectrum in Ångstrom units [3] :—

Spark : Ultra-violet : 2709·05, 2813·84, 3649·8 ; Visible : 3814·6, 4340·83, 4436·49, 4533·33, 4682·36, 4826·12, 4856·25, 5400·31, 5406·78, 5502·07, 5601·72, 5616·73, 5660·81, 5729·2, 5958·4, 6167·4, 6200·6, 6446·3.

Arc : Visible : 3814·6, 4682·4.

Runge and Precht studied the flame spectrum of radium and obtained the following as the most important lines [4] :—

Flame : 4826 ; strong bands between 6130 and 6330 ; 6349 ; strong band between 6530 and 6700 ; 6653 Å.

The fluorescent light from radium compounds gives a banded spectrum of nitrogen superimposed on a faint continuous spectrum due to the fluorescence of the crystals. In an evacuated tube no nitrogen bands are obtained, and in an atmosphere of helium three helium lines are observed.[5]

The Atomic Weight of Radium.—*The Approximate Atomic Weight.*—Radium belongs to the alkaline earth group of metals, and, therefore, it should be divalent. This has been verified by electro-endosmotic measurements,[6] and by diffusion experiments.[7]

From a study of the spectrum Runge and Precht concluded that the atomic weight should be about 258,[8] but by a different formula Watts deduced 226·56 from the same data.[9] Measurements of the electrical conductivity of radium bromide solutions indicated that the former was probably too high.[10] From consideration of the numerical relationships of the Periodic Table, Wilde concluded that the atomic weight should be approximately 184.[11]

The Exact Atomic Weight.—The first chemical determination of the atomic weight was undertaken by Mme. Curie.[12] Samples of radio-active barium chloride of gradually increasing activity were precipitated

[1] Curie and Debierne, *loc. cit.*

[2] de Forcrand, *Ann. Chim. Phys.*, 1911, [8], 24, 256.

[3] Marshall Watts, *Index of Spectra* (Wesley & Son, London ; Abel Heywood & Son, Manchester), Appendix " V," 1911 ; see also Runge, *Ann. Physik*, 1900, 2, 742 ; Runge and Precht, *ibid.*, 1903, 12, 407; Crookes, *Proc. Roy. Soc.*, 1904, 72, 295 ; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1911, 120, 967.

[4] Runge and Precht, *Ann. Physik*, 1903, 10, 655 ; see also Precht, *Jahrb. Radioakt. Elektron.*, 1904, 1, 61.

[5] Huggins and Huggins, *Proc. Roy. Soc.*, 1903, 72, 196, 409 ; 1905, 76A, 488 ; 1906, 77A, 130 ; Himstedt and Meyer, *Le Radium*, 1905, 2, 385 ; *Physikal. Zeitsch.*, 1905, 6, 688 ; 1906, 7, 762 ; Walter, *Ann. Physik*, 1905, 17, 367 ; 1906, 20, 327 ; Pohl, *ibid.*, 1905, 17, 375 ; Walter and Pohl, *ibid.*, 1905, 18, 406 ; Marckwald and Hermann, *Ber. Deut. physikal. Ges.*, 1905, 7, 227.

[6] Freundlich and Elissafoff, *Physikal. Zeitsch.*, 1913, 14, 1051.

[7] von Hevesy, *Phil. Mag.*, 1913, [6], 25, 390 ; *Physikal. Zeitsch.*, 1913, 14, 49.

[8] Runge and Precht, *Physikal. Zeitsch.*, 1903, 4, 285.

[9] Watts, *Phil. Mag.*, 1909, [6], 18, 411 ; see also Rudorf, *Zeitsch. physikal. Chem.*, 1905, 50, 100.

[10] Kohlrausch and Henning, *Ann. Physik*, 1906, [4], 20, 96.

[11] Wilde, *Phil. Mag.*, 1908, [6], 15, 280.

[12] Mme. Curie, *Compt. rend.*, 1899, 129, 760 ; 1900, 131, 382.

with silver chloride. With the weakest of these, values for the atomic weight were obtained which were not materially different from the atomic weight of barium. As the activity increased, however, the atomic weight also began to increase. At the same time the product was examined spectroscopically.[1] When the radium and barium spectra were of almost equal intensity the atomic weight was 173·8. Ultimately a product was obtained which contained only a trace of barium and had an atomic weight of 225.

In 1902 a sample of radium chloride, which still showed the three principal barium lines with considerable intensity, gave values lying between 220 and 224. For all these determinations the same sample of radium chloride was used, the radium being recovered from the solution and retransformed into chloride. After further purification of the salt three more determinations were made with the following results [2] :—

Experiment.	Anhydrous Radium Chloride.	Silver Chloride.	Atomic Weight of Radium.
	grm.	grm.	
I.	0·09192	0·08890	225·56
II.	0·08936	0·08627	226·06
III.	0 08839	0·08589	224·10
			Mean = 225·2

Fresh determinations were made in 1907.[3]

Experiment.	Anhydrous Radium Chloride.	Silver Chloride.	Atomic Weight of Radium.
	grm.	grm.	
I.	0·4052	0·3906−0·00006	226·5
II.	0·4020	0·3879−0·00006	226·2
III.	0·39335	0·3795−0·00006	226·3
			Mean = 226·3

0·00006 grm. = weight of filter ash.

Later, Thorpe, with somewhat small quantities of the chloride, obtained the following results [4] :—

Experiment.	Anhydrous Radium Chloride.	Silver Chloride.	Atomic Weight of Radium.
	grm.	grm.	
I.	0·0627	0·0604	226·7
II.	0·0639	0·0618	225·4
III.	0·0784	0·0753	227·5

[1] Demarçay, Compt. rend., 1898, 127, 1218; 1899, 129, 716; 1900, 131, 258.
[2] Mme. Curie, ibid., 1902, 135, 161; Ann. Chim. Phys., 1903, [7], 30, 137. All the atomic weights given have been recalculated on the basis Ag=107·88, Cl=35·457, Br =79·916, which are the values used throughout the series.
[3] Mme. Curie, Compt. rend., 1907, 145, 422; Jahrb. Radioakt. Elektron., 1909, 6, 38.
[4] Thorpe, Proc. Roy. Soc., 1908, 80A, 298.

hydride ought to be a compound having a heat of formation of 35·4 Cal., and temperature of dissociation 900° C. He further stated that it should react with water with the evolution of 54·6 Cal.[1]

Radium Chloride, RaCl₂, may be obtained as the dihydrate, $RaCl_2.2H_2O$, by dissolving the carbonate in hydrochloric acid and allowing to crystallise. It may be dehydrated by heating to 100° C. in a platinum crucible for several hours, but it is not decomposed if the temperature be raised to 200° C. It is less soluble in water than barium chloride, and is precipitated by hydrochloric acid and by alcohol.[2,3]

According to de Forcrand,[1] the heat of formation should be 197·0 Cal., and the heat of solution zero.

Radium chloride is paramagnetic.[3]

Radium Bromide, RaBr₂, may be formed by the action of hydrobromic acid solution on the carbonate and subsequent crystallisation as the dihydrate, $RaBr_2.2H_2O$, isomorphous with barium bromide dihydrate.[4] It gives up bromine on exposure to the air and becomes alkaline, forming the hydroxide and ultimately the carbonate.[5]

Radium bromide is less volatile than barium bromide which volatilises at 820° C., and it is possible that a separation of the two might be effected by this method.[6]

The molecular heat of formation of anhydrous radium bromide is probably about 180 Cal., and the heat of solution 2 Cal.[1]

It is more soluble in water than the chloride.

Measurements of the electrical conductivity of radium bromide solutions have been made. The mobility of $\frac{1}{2}Ra$ was found to be 58, and the temperature coefficient at 18° C. 0·024. Solutions of different concentrations were examined with the following results [7] :—

Gram-equivalents per Litre (assuming at. wt. 225.)	Equivalent Conductivity.	Temperature Coefficient.
0 04901	99·5	0·0221
0 01713	106 8	..
0 008395	111·0	..
0·001356	118 3	0 225
0·000712	120·1	..
0 0003043	122·2	..
0 0000872	124·1	..
At infinite dilution	Approx. 125	..

There is some evidence of the existence of the compound $2BaBr_2.RaBr_2.6H_2O$.[8]

[1] de Forcrand, *Ann. Chim. Phys.*, 1911, [8], **24**, 256.
[2] Mme. Curie, *Thèse présentée a la Faculté des Sciences de Paris*, 1903, English translation reprinted from *Chem. News*, 1904 ; Hönigschmid, *Monatsh.*, 1912, **33**, 253.
[3] Mme. Curie, *Traité de Radioactivité* (Gauthier-Villars), 1910, Tome I, p. 174.
[4] Rinne, *Zentr. f. Miner. Geol.*, 1903, 134 ; *Jahrb. Radioakt. Elektron.*, 1906, **3**, 239 ; Mme. Curie, *loc. cit.*
[5] Giesel, *Ber.*, 1902, **35**, 3608 ; Ramsay, *Monatsh.*, 1908, **29**, 1013 ; Porter, *Nature*, 1907, **76**, 151 ; Egerton, *ibid.*, 174.
[6] Stock and Heyneman, *Ber.*, 1909, **42**, 4088.
[7] Kohlrausch and Henning, *Chem. Zentr.*, 1904, ii, 296 ; *Ann. Physik*, 1906, [4], **20**, 96.
[8] Scholl, *J. Amer. Chem. Soc.*, 1920, **42**, 889.

Radium Iodide and Fluoride have not been isolated. De Forcrand gives as their probable heats of formation 151·6 and 225·6 Cal. respectively, and of solution 6·4 and 0·8 Cal.[1]

Radium Iodate, Ra(IO₃)₂.—According to Denigès, radium may be distinguished microchemically from barium by the use of a 10 per cent. iodic acid solution with a 0·3 per cent. solution of the salt. Typical and distinct precipitates are obtained.[2]

Radium Oxide does not appear to have been isolated. Its heat of formation would probably be 113·2 Cal., and its heat of solution 46 Cal.[1]

Radium Hydroxide, Ra(OH)₂.—Radium dissolves in water with the formation of radium hydroxide solution.[3] As already mentioned, the fractional separation of the hydroxide has been proposed for the purification of radium salts from barium.

Radium Sulphate, RaSO₄, may be obtained by precipitation of a soluble radium salt by sulphuric acid or a sulphate. It is a very insoluble compound, its solubility at 25° C. being $2 \cdot 1 \times 10^{-8}$ grm. per c.c., about 100 times less than that of barium sulphate.[4] The presence of sulphuric acid up to 50 per cent. has no appreciable influence on the solubility, but at higher concentrations this increases rapidly, as observed in the case of the other alkaline earths. In 70 per cent. acid it is more than 12 times greater than in 60 per cent. acid. Increase of temperature also causes a large increase of solubility in dilute acid solutions.

Much attention has been directed to the behaviour of radium sulphate in the presence of barium sulphate. When barium sulphate is completely precipitated from a solution containing a radium salt, the latter is also carried down, although the solubility product $C_{\mathrm{Ra}} \cdot \times C_{\mathrm{SO}_4''}$ may not be attained.[5]

Paneth pointed out that radio-elements are readily adsorbed by analogous compounds which are sparingly soluble in the solvent.[6] Germann found that the adsorption laws are strictly valid for radium salts in contact with barium sulphate, but if the barium sulphate is precipitated in a radium solution all the radium is adsorbed, because, the particles at first being of molecular dimensions, the adsorbing surface is enormous.[7] This result, however, is not in agreement with the statement of Lind and his colleagues, that when a radium-barium solution is precipitated by sulphuric acid or a soluble sulphate the ratio of radium to barium in the precipitate is the same as in the original solution. This behaviour is comparable with that of isotopic elements,[8] although radium and barium are not isotopic. This phenomenon they denoted by the term pseudo-isotopy. A suggested explanation is that radium and barium sulphates are isomorphous, and, therefore, form a solid solution.[9]

Radium Carbonate, RaCO₃, may be obtained by fusion of the sulphate with an alkali carbonate, or by boiling with a solution of the

[1] de Forcrand, *loc. cit.*
[2] Denigès, *Compt. rend.*, 1920, **171**, 633.
[3] Curie and Debierne, *ibid.*, 1910, **151**, 523.
[4] Lind, Underwood, and Whittemore, *J. Amer. Chem. Soc.*, 1918, **40**, 465.
[5] Ebler and van Rhyn, *Ber.*, 1921, **54B**, 2896.
[6] Paneth, *Physikal. Zeitsch.*, 1914, **15**, 924.
[7] Germann, *J. Amer. Chem. Soc.*, 1921, **43**, 1615.
[8] See section on Isotopes.
[9] Soddy, *Chem. Soc. Ann. Rep.*, 1919, **15**, 219.

latter. It may also be precipitated from solutions of soluble radium salts by ammonium carbonate. It is insoluble in water, but dissolves readily in hydrochloric acid.

Radium might be concentrated in mixtures of the alkaline earths by fractional precipitation of the carbonates, radium being precipitated last.[1]

Radium Nitride, Ra_3N_2.—Radium absorbs nitrogen, probably even more readily than barium,[2] forming a blackish compound which is no doubt a nitride.[3]

Radium Azide, $Ra(N_3)_2$.—This compound has already been mentioned in connection with the separation of metallic radium. According to Ebler it is a fairly stable, crystallisable compound.[2] On being heated *in vacuo* below 100° C. for several hours, it begins to decompose, giving nitrogen.

Radium Nitrate, $Ra(NO_3)_2$.—The solubility of radium nitrate is probably about the same as that of barium nitrate.[4]

Radium Silicate.—Radium salts are apparently adsorbed by gelatinous silica.[5] It is possible that the silicate may be formed. The acidity of the solution plays an important part, since acid exerts a desorbent action, the process possibly being represented by the equation,

$$RaSiO_3 + 2HCl = RaCl_2 + H_2SiO_3.$$
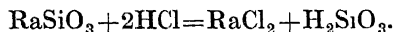
Radium Platinocyanide may be obtained as a green salt which rapidly becomes dichroic in solution.[6]

Other Salts.—According to Denigès, the microchemical precipitates of radium fluosilicate, oxalate, tartrate, ferrocyanide, cyanurate, and phosphomolybdate are identical in appearance with the corresponding salts of barium.[7]

By a consideration of the relationships between the different metals of the alkaline earth group, de Forcrand predicted some of the properties of radium salts which have not actually been determined experimentally.[8]

Detection and Estimation of Radium.—Radium salts colour the flame carmine red.[9] The most characteristic lines in the spectrum are 6653, 6600, 6300, and 4826 Å.[10]

The detection of radium microchemically as the iodate has already been mentioned.

There is a considerable difference between the tensions of decomposition of barium and radium compounds, so that it is possible that they might be separated electrochemically.[11]

Radium, however, is best detected and estimated by radioactive measurements,[12] especially by determinations of the amount of emanation evolved.[13]

[1] Giesel, *Ber.*, 1902, **35**, 3608.
[2] Ebler, *ibid.*, 1904, **37**, 811.
[3] Curie and Debierne, *Compt. rend.*, 1910, **151**, 523.
[4] Mme. Curie, *Traité de Radioactivité* (Gauthier-Villars), 1910, Tome I, p. 174.
[5] Wojtasrewski, *Le Radium*, 1913, **10**, 363 (Abs.).
[6] Giesel, *Wied. Annalen*, 1899, **69**, 91 ; *Ber.*, 1902, **35**, 3608.
[7] Denigès, *Compt. rend.*, 1920, **171**, 633.
[8] de Forcrand, *ibid.*, 1911, **152**, 66.
[9] Giesel, *Physikal. Zeitsch.*, 1902, **3**, 578 ; Runge and Precht, *Ann. Physik*, 1903, **10**, 655.
[10] Runge and Precht, *loc. cit.*
[11] Berthier, *Le Radium*, 1904, **1**, 48.
[12] Rutherford, *Radioactive Substances and their Radiations* (Cambridge University Press), 1913, p. 657.
[13] Eve, *Le Radium*, 1905, **2**, 136.

RADIOACTIVE PHENOMENA.

The characteristic of radium which sharply distinguishes it from the other members of the alkaline earth group, and the discovery of which has been of supreme importance to the development of physical and chemical theory, is the property of undergoing spontaneous degradation to a different element of the same or lower atomic weight, with the emission of radiations capable of producing certain striking chemical and physical phenomena. This property is shared by thorium [1] and uranium,[2] metals known before the discovery of radium, and also by a number of elements discovered since, some of which are of a very transitory nature.

The radiations given out may be of three types, known as α-, β-, and γ-rays.

α-**Rays** consist of positively charged particles of helium [3] of similar corpuscular nature to the canal rays in a vacuum electric discharge tube, and deviable by a powerful magnetic or electrostatic field.[4] Their initial velocity is of the order of 2×10^9 cm. per sec.,[5] and the large kinetic energy which they thus possess is the cause of the physical and chemical effects which they produce.

The α-rays ionise by shock the particles of air they encounter through a range of several centimetres at atmospheric pressure, and thus make the air a conductor of electricity.[6] The velocity and range are related by the formula $V^3 = aR$, where " V " is the velocity, " a " a constant, and " R " the range.[7]

The α-rays can also penetrate thin sheets of solid matter, such as aluminium, of thickness of the order of 0·0004 cm.,[8] the range in different materials being dependent on the atomic weight of the substance,[9, 10] and the relative absorption increasing as the rays approach the end of their range.[10]

[1] See Vol. V.

[2] See Vol. VII.

[3] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, 204 ; 1904, **73**, 346 ; Rutherford and Geiger, *ibid.*, 1908, **81A**, 162 ; Rutherford and Royds. *Phil. Mag.*, 1909, [6], **17**, 281.

[4] Strutt, *Phil. Trans.*, 1901, **196A**, 507 ; Crookes, *Proc. Roy. Soc.*, 1902, **69**, 413 ; Becquerel, *Compt. rend*, 1903, **136**, 199 ; Des Condres, *Physikal. Zeitsch.*, 1903, **4**, 483 ; Rutherford, *ibid.*, 1903, **4**, 235 ; *Phil. Mag.*, 1903, [6], **5**, 177 ; Boltwood and Rutherford, *ibid.*, 1911, [6], **22**, 586.

[5] Mackenzie, *Phil. Mag.*, 1905, [6], **10**, 538 ; Rutherford, *ibid.*, 1906, [6], **12**, 134, 348 ; Rutherford and Hahn, *ibid.*, 371 ; Geiger and Nuttall, *ibid.*, 1911, [6], **22**, 613 ; 1912, [6], **24**, 647 ; Huff, *Proc. Roy. Soc*, 1906, **78A**, 77.

[6] Rutherford, *Phil. Mag.*, 1899, [5], **47**, 109 ; 1900. [5], **49**, 161 ; Owens, *ibid.*, 1900, [5], **48**, 360 ; Mme. Curie, *Compt. rend.*, 1900, **130**, 76 ; Strutt, *Phil. Trans*, 1901, **196A**, 507 ; Rutherford and Brooks, *Phil. Mag.*, 1902, [6], **4**, 1 ; Meyer and Schweidler, *Sitzungsber. K. Akad. Wiss. Wien*, 1906, **115**, 713 ; Bragg and Kleeman, *Phil. Mag.*, 1904, [6], **8**, 726 ; Bragg, *ibid.*, 1907, [6], **13**, 333 ; McClung, *ibid.*, 1906, [6], **11**, 131 ; Taylor, *ibid.*, 1911, [6], **21**, 571 ; Rutherford and Geiger, *Proc. Roy. Soc*, 1908, **81A**, 141 ; Geiger, *ibid.*, 1909, **82A**, 486 ; and others.

[7] Geiger, *ibid.*, 1910, **83A**, 505.

[8] Rutherford, *Phil. Mag.*, 1899, [5], **47**, 109 ; Owens, *loc. cit.* ; Rutherford and Brooks, *loc. cit.* ; Meyer and Schweidler, *loc. cit.*

[9] Bragg and Kleeman, *Phil. Mag.*, 1905, [6], **10**, 318 ; Bragg, *ibid.*, 1905, [6], **10**, 600 ; 1906, [6], **11**, 617 ; Rutherford, *ibid.*, 1906, [6], **12**, 134 ; Meyer, *Physikal. Zeitsch.*, 1906, **7**, 917 ; Kučera and Mašek, *ibid.*, 1906, **7**, 630 ; Adams, *Phys. Review*, 1907, **24**, 108 ; Bragg and Cooke, *Phil. Mag.*, 1907, **14**, 425 ; Bragg, *ibid.*, 1907, **13**, 507 ; Taylor, *ibid.*, 1909, **18**, 604 ; *Amer. J. Sci.*, 1909, **28**, 357.

[10] Curie, *Compt. rend.*, 1900, **130**, 76.

The absorption of α-rays is accompanied by a notable evolution of heat, which can be measured calorimetrically, and which is due to the conversion of the kinetic energy of the α-particles into heat energy.[1]

When exposed to the action of α-rays, phosphorescent substances, such as zinc sulphide, diamond, barium platinocyanide, fluorspar, and kunzite, become brightly luminous, and on examination under the microscope this luminosity is found to be made up of small flashes of light, each flash being produced by the shock of an α-particle against the phosphorescent substance.[2] α-Particles may be counted by the number of flashes produced.[3]

It can also be shown that each α-particle produces a photographic effect.[4]

α-Rays can bring about a number of chemical reactions. Water is decomposed by them,[5] the nature of the decomposition products depending upon the conditions. At $-183°$ C., apparently, pure hydrogen and oxygen are formed. In the liquid state first hydrogen in excess is evolved and hydrogen peroxide formed, and then oxygen in excess is produced.[6] The reaction is intimately connected with the ionisation produced by the radiation.[6, 7]

Other compounds are also decomposed—carbon monoxide, carbon dioxide, hydrogen sulphide, ammonia, nitrous oxide, hydrogen iodide, organic iodine compounds, purines, etc.[8] Recombination of gases may be effected—for example, oxygen with hydrogen,[9] nitrogen with hydrogen,[10] and oxygen may form ozone.[11] Carbon monoxide is reduced by hydrogen under the influence of radium emanation.[12] The α-rays have also a catalytic effect on certain oxidation reactions.[13]

Colorations are produced in minerals and other substances by α-rays

[1] Becquerel, *Compt. rend.*, 1899, 129, 912 ; Bary, *ibid.*, 1900, 130, 776 ; Giesel, *Ber.*, 1903, 36, 2368 ; Curie and Laborde, *Compt. rend.*, 1903, 136, 673 ; Rutherford and Barnes, *Phil. Mag.*, 1904, [6], 7, 202 ; Ångström, *Physikal. Zeitsch.*, 1905, 6, 685 ; *Le Radium*, 1905, 2, 375; Pegram and Webb, *Phys. Review*, 1908, 27, 18 ; Poole, *Phil. Mag.*, 1910, [6], 19, 314 ; 1912, [6], 23, 183 ; Rutherford and Robinson, *ibid.*, 1913, [6], 25, 312 ; Duane, *Le Radium*, 1910, 7, 260; *Compt. rend.*, 1910, 151, 379; von Schweidler and Hess, *Sitzungsber. K. Akad Wiss. Wien*, 1908, 117, 879 : Hess, *ibid.*, 1912, 121, 1419; Callendar, *Proc. Phys. Soc.*, 1911, 23, 1.

[2] Giesel, *Ber*, 1902, 35, 3608 ; 1903, 36, 342 ; Crookes, *Proc. Roy. Soc.*, 1903, 71. 405 ; 1904, 74, 47 ; Elster and Geitel, *Physikal. Zeitsch.*, 1903, 4, 439.

[3] Regener, *Ber. Deut. physikal. Ges.*, 1908, 19, 78; Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, 81A, 156.

[4] Kinoshita, *ibid.*, 1909, 83A, 432.

[5] Cameron and Ramsay, *Trans. Chem. Soc.*, 1908, 93, 966 ; Debierne, *Compt. rend*, 1909, 148, 703 ; *Le Radium*, 1909, 6, 65 ; *Ann. Physique*, 1914, [9], 2, 97 ; Bergwitz, *Physikal. Zeitsch*, 1910, 11, 273.

[6] Duane and Scheuer, *Le Radium*, 1913, 10, 33.

[7] Lind, *J. Physical Chem.*, 1912, 16, 564 ; *Le Radium*, 1912, 9, 426 ; *J. Amer. Chem. Soc.*, 1919, 41, 531 ; *Trans. Amer. Electrochem. Soc.*, 1918, 34, 211.

[8] Pellini and Vaccari, *Atti R. Accad. Lincei*, 1904, [5], 13, 11. 269 ; Ramsay, *Trans. Chem. Soc.*, 1907, 91, 931 ; Cameron and Ramsay, *ibid.*, 1908, 93, 966, 992 ; Perman, *ibid.*, 1911, 99, 132 ; Usher, *ibid.*, 1910, 97, 389, 1193 ; Lind, *Le Radium*, 1911, 8, 289 ; *Amer. Chem. J.*, 1912, 47, 397 ; Wourtzel, *Compt. rend.*, 1913, 157, 929 ; 1914, 158, 571 ; *Le Radium*, 1914–19, 11, 289, 332 ; Mesernitsky, *ibid.*, 1912, 9, 145.

[9] Cameron and Ramsay, *loc. cit.* ; Scheuer, *Compt. rend.*, 1914, 159, 423 ; Lind, *J. Amer. Chem. Soc.*, 1919, 41, 531 ; Davis and Edwards, *J. Soc. Chem. Ind.*, 1905, 24, 266.

[10] Usher, *loc. cit.*

[11] M. and Mme. Curie, *Compt. rend.*, 1899, 129, 823 ; Curie and Debierne, *ibid.*, 1910, 150, 386 ; Lind, *Le Radium*, 1912, 9, 104.

[12] Scheuer, *Compt. rend.*, 1914, 158, 1887.

[13] Lemay and Jaloustre, *ibid.*, 1921, 173, 916.

—for example, rock salt,[1] fluorspar,[1] quartz,[2] and other minerals,[3] and also glass,[4] ordinary soda-glass being coloured deep violet, and other kinds brown or yellow. In some kinds of mica—biotite, condierite, and muscovite—minute coloured spherical areas have been detected, showing pleochroism under polarised light and hence called "pleochroic haloes." They are due to the coloration of the mica by the α-rays from a small central fragment of radioactive matter.[5] Joly found that the diameter of this nuclear particle was often less than 5×10^{-4} cm., its mass probably being of the order of 5×10^{-10} grm.[6]

This chemical action is the basis of the physiological effects of radium produced by all the radiations. As the earlier workers soon found, it destroys the living tissues by its corrosive action on the skin, and it has therefore been applied in the treatment of skin diseases and of malignant growths.[7] The action on plants and seeds has also been studied. A brief exposure may produce a favourable effect, but too long an exposure kills.[8]

Not only, however, are the α-particles able to bring about the decomposition of chemical compounds, but they have proved to be a source of sufficient energy to cause the breakdown of some of the chemical elements. From nitrogen, for example, hydrogen atoms have been obtained.[9]

The properties of the α-rays may be used for their detection. For this purpose their ionising power, and hence their ability to discharge a charged electroscope, is most frequently used, but their action on a zinc sulphide screen, or on a photographic plate, may also be employed.[10]

β-Rays, which were first observed by Giesel,[11] consist of negative electrons, and are comparable with the cathode rays obtained by the electric discharge in vacuum tubes. The velocity of the β-rays is greater than that of the cathode rays, however, and may even reach to within 1 or 2 per cent. of the velocity of light.[12] They are strongly deflected by a magnetic field,[13] and since the amount of deflection depends on the velocity of the rays, they can be analysed by this method, the radiations

[1] Giesel, *Ber. Deut. physikal. Ges.*, 1900, 2, 9; Henrich, *Zeitsch. angew. Chem.*, 1920, 33, 5, 13, 20.

[2] Salomonsen and Dreyer, *Compt. rend.*, 1904, 139, 533; Berthelot, *ibid.*, 1907, 145, 818.

[3] Doelter, *Le Radium*, 1910, 7, 58.

[4] Observed by all investigators in radioactivity; see Lind, *J. Phys. Chem.*, 1920, 24, 437.

[5] Joly, *Phil. Mag.*, 1907, [6], 13, 381; 1910, 19, 327; Joly and Fletcher, *ibid.*, 1910, [6], 19, 630.

[6] Joly, *Radioactivity and Geology* (Constable), 1909; see also section on Radium and Geology.

[7] Information on this point must be sought in physiological and medical literature.

[8] Stoklasa, *Compt. rend.*, 1912, 155, 1096; see Soddy, *Ann Rep. Chem. Soc.*, 1912, 9, 324; 1913, 10, 287.

[9] Rutherford, *Phil. Mag.*, 1919, [6], 37, 537, 562, 571, 581; *Proc. Roy. Soc.*, 1920, 97A, 374; *Trans. Chem. Soc.*, 1922, 121, 400.

[10] See Rutherford, *Radioactive Substances and Their Radiations* (Cambridge University Press), 1913; Mme. Curie, *Traité de Radioactivité* (Gauthier-Villars), 1910.

[11] Giesel, *Ann. Physik*, 1899, 69, 834; see also Elster and Geitel, *ibid.*, 88; Meyer and von Schweidler, *Physikal. Zeitsch.*, 1899, 1, 90, 113; Becquerel, *Compt. rend.*, 1899, 129, 997, 1205; Curie, *ibid.*, 1900, 130, 73.

[12] Kaufmann, *Physikal. Zeitsch.*, 1902, 4, 55; *Ann. Physik*, 1906, 19, 487; Bucherer, *ibid.*, 1909, 28, 513; 29, 1063.

[13] Curie, *Compt. rend.*, 1900, 130, 76; Rutherford and Grier, *Phil. Mag.*, 1902, [6], 4, 315.

from single substances being found to be complex.[1]   They ionise the air, but not to so great an extent as the α-rays,[2] and the same may be said of their effect on a phosphorescent screen.[3]   Their photographic action, however, is greater than that of the α-rays.[4]

The β-rays are much less active chemically than the α-rays,[5] but changes are nevertheless produced by them.   White phosphorus is transformed to red,[6] iodoform is decomposed,[7] hydrogen and chlorine may be made to combine,[8] the rate of crystallisation of sulphur is increased,[9] water is decomposed,[10] and hydrogen arsenide is oxidised to arsenious acid.[11]

β-Rays have much greater penetrating power than α-rays.[12]   The penetrating power varies greatly, owing to the great variation in velocity, but in some cases the intensity is not diminished by much more than one-half, even by passage through nearly a millimetre of aluminium.[13]

The heating effect of the β-rays is very small.[14]

γ-Rays.—The third type of radiation given by radioactive substances is similar to the X-rays, but much more penetrating, and therefore consists of extremely short wave-lengths, probably of the order of $0 \cdot 1$ to $0 \cdot 01$ Å.[15]   They were first observed by Villard,[16] using a photographic method, and he also showed that they were not deflected by a magnetic field.[17]   The intensity of the γ-rays from radium is only reduced to half-value by passage through lead 1 cm. thick.[18]   The absorption coefficient diminishes as the absorption increases.   In air the intensity is reduced to one-half after a distance of 115 metres at normal temperature and pressure.[19]   In their passage through matter γ-rays produce a secondary β- and γ-radiation.[20]

[1] Danysz, Le Radium, 1912, 9, 1 ; Danysz and Gotz, ibid., 6 ; Baeyer, Hahn, and Meitner, Physikal. Zeitsch., 1912, 13, 264 ; Baeyer, ibid., 485.
[2] Durack, Phil. Mag., 1903, [6], 5, 550 ; Eve, ibid., 1911, [6], 22, 551 ; Geiger and Kovarik, ibid., 1911, [6], 22, 604.
[3] Becquerel, Compt. rend., 1899, 129, 912 ; Regener, Ber. Deut. physikal. Ges., 1908, 19, 351.
[4] Soddy, Trans. Chem. Soc., 1902, 81, 860.
[5] Usher, Jahrb. Radioakt. Elektron., 1911, 8, 323.
[6] Becquerel, Compt. rend., 1901, 133, 709.
[7] Hardy and Wilcock, Proc. Roy. Soc., 1903, 72, 200.
[8] Jorissen and Ringer, Ber., 1906, 39, 2093.
[9] Frischauer, Compt. rend., 1909, 148, 1251.
[10] Debierne, ibid., 1909, 148, 703 ; Le Radium, 1909, 6, 65 ; Kernbaum, Compt. rend., 1909, 148, 705 ; Le Radium, 1909, 6, 225, 352.
[11] Reckleben and Lockemann, Zeitsch. anorg. Chem., 1915, 92, 145.
[12] Rutherford, Phil. Mag., 1899, [5], 47, 109.
[13] Hahn, Zeitsch. Elektrochem., 1910, 16, 606 ; Schmidt, Physikal. Zeitsch., 1906, 7, 764 ; 1907, 8, 361 ; 1909, 10, 6, 929 ; 1910, 11, 262 ; Hahn and Meitner, ibid., 1908, 9, 321, 697 ; 1909, 10, 741 ; Baeyer, Hahn, and Meitner, ibid., 1911, 12, 378 ; Meitner, ibid., 1915, 16, 272 ; Godlewski, Phil. Mag., 1905, [6], 10, 375.
[14] Rutherford and Robinson, Phil. Mag., 1913, 25, 312 ; see also Eve, ibid., 1911, [6], 22, 560.
[15] Rutherford, Phil. Mag., 1917, [6], 34, 153 ; Kohlrausch, Physikal. Zeitsch., 1918, 19, 345 ; Glocker, ibid., 66.
[16] Villard, Compt. rend., 1900, 130, 1010, 1178.
[17] See also Becquerel, ibid., 1900, 130, 1154.
[18] Mr. and Mrs. Soddy, and Russell, Phil. Mag., 1910, [6], 19, 725 ; see also Rutherford, Physikal. Zeitsch., 1902, 3, 517 ; Wigger, Jahrb. Radioakt. Elektron., 1905, 2, 420 ; McClelland, Phil. Mag., 1904, [6], 8, 67 ; Eve, ibid., 1908, [6], 16, 224 ; 1909, 18, 275 ; Soddy and Russell, ibid., 1909, 18, 620 ; Tuomikoski, Physikal. Zeitsch., 1909, 10, 372.
[19] Chadwick, Proc. Physical Soc., 1912, 24, 152 ; see also Hess, Physikal. Zeitsch., 1911, 12, 998 ; Kohlrausch, ibid., 1918, 19, 345.
[20] Eve, Phil. Mag., 1904, [6], 8, 669 ; see also Bragg and Madsen, ibid., 1908, [6], 15, 663 ; 1908, [6], 16, 918 ; Hackett, Trans. Roy. Dub. Soc., 1909, 9, 201.

γ-Rays ionise the air, but to a much less extent than α-rays.

The chemical action of the γ-rays is less important than that of the α-rays, or even of the β-rays, and often very small in comparison with the effect produced by light and ultra-violet rays.[1]

Both liquid and solid dielectrics become partial conductors under the action of the penetrating rays of radium.[2]

The heating effect of γ-rays is small compared with that of α-rays.[3]

β- and γ-rays have effects on colloids similar to those produced by minute traces of electrolytes in amount insufficient for immediate coagulation.[4]

From a comparative study of characteristic X-rays and γ-rays it seems probable that the γ-rays result from the action of β-rays on the inner rings of the electrons contained in the nucleus.[5]

The power of giving off these three kinds of radiation which radio-active substances possess, is an atomic phenomenon, and is not affected in any way by the type of chemical combination into which the atom may enter. Neither is the rate of emission of radiation affected by temperature, at least within the range from the temperature of liquefaction of hydrogen[6] to about 2500° C.[7, 8, 9] Variations, at first supposed to be observed in the β-ray activity in certain cases, were later found to be due to the volatility of the substances under consideration.[9]

The effect of pressure, up to 2000 atmospheres, has also been tried with negative results.[8, 10]

The emission of energy by an atom, in the form of α-, β-, or γ-rays, must naturally be accompanied by some change in the atom itself. In the case of the α-ray, which is a material particle, the mass of the atom must be decreased, and thus a new element of lower atomic weight be left. Emission of β- and γ-rays must result in a change in the energy content of the atom, and therefore again a new atom is formed although of the same atomic weight as the old. Thus radioactive changes, being spontaneous changes taking place within the atom of the element in question, and being unaffected by its chemical relationships, may be regarded as of the nature of true monomolecular reactions. Indeed, it is possible that they may be looked upon as the only cases of monomolecular reactions which come under no suspicion of being other than they appear.[11] The reaction taking place might be represented as follows :—

$$A = \alpha\text{-particle} + B$$
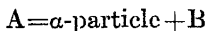
[1] Kailan, *Monatsh.*, 1911, 32, 1019 ; 1912, 33, 71, 1329, 1361 ; 1913, 34, 359, 1245, 1269 ; 1914, 35, 859 ; 1921, 42, 387 ; *Zeitsch. physikal. Chem.*, 1920, 95, 215 ; 1921, 98, 474.

[2] Curie, *Compt. rend.*, 1902, 134, 420 ; Becquerel, *ibid.*, 1903, 136, 1173 ; Becker, *Ann. Physik*, 1903, 12, 124 ; Bohm-Wendt and von Schweidler, *Physikal. Zeitsch.*, 1909, 10, 379 ; Bialobjeski, *Compt. rend.*, 1909, 149, 279 ; *Le Radium*, 1910, 7, 48, 76 ; 1911, 8, 293.

[3] Rutherford and Barnes, *Phil. Mag.*, 1905, [6], 9, 621 ; Rutherford and Robinson, *ibid.*, 1913, [6], 25, 312 ; Eve, *ibid.*, 1911, [6], 22, 560.

[4] Fernau and Pauli, *Kolloid. Zeitsch.*, 1917, 20, 20.

[5] See Soddy, *Ann. Rep. Chem. Soc*, 1918, 15, 211.

[6] Curie and Onnes, *Le Radium*, 1913, 10, 181.

[7] Bronson, *Proc. Roy. Soc.*, 1906, 78A, 494 ; Makower, *ibid.*, 1906, 77A, 241 ; Makower and Russ, *ibid.*, 1907, 79A, 158 ; Schmidt, *Physikal. Zeitsch.*, 1908, 9, 113 ; Schmidt and Cermak, *ibid.*, 1910, 11, 793 ; Engler, *Ann. Physik*, 1908, 26, 483.

[8] Rutherford and Petavel, *Brit. Assoc. Rep.*, 1907, Section A, 456.

[9] Russell, *Proc. Roy. Soc.*, 1911, 86A, 240.

[10] Eve and Adams, *Nature*, 1907, 76, 269 ; Schuster, *ibid.*, 1907, 76, 269.

[11] Lowry, *Trans. Faraday Soc.*, 1922, 17, 596.

where the element A changes into the element B with the emission of an α-particle. If B is also radioactive and emits either α- or β-rays—γ-rays only appear accompanying β-rays and are probably due to the latter[1]—it will change into a fresh substance C, and so on. This is an example of consecutive monomolecular reactions. The amount of B present at any moment will depend on the difference in the rates of change of A and B.

Radioactive Constants.—In a monomolecular reaction the rate of change at any moment is proportional to the amount of the original substance present—that is, if N be the number of atoms of a radioactive substance present at the time "t"

$$-\frac{dN}{dt} = \lambda N,$$

where "λ" is the radioactive constant, or fraction disintegrating in unit time.

Integrating between the time limits 0 and "t," the number of atoms "N" at the time "t" is obtained in terms of "N_0" the initial quantity present, "λ," and "t," that is

$$N = N_0 e^{-\lambda t},$$

or, expressed more conveniently in terms of logarithms,

$$\log_{10} \frac{N}{N_0} = -\cdot 4343 \lambda t.$$

This represents the case of one radioactive change, A to B for instance, without considering the fate of B. The equations representing successive changes are much more complicated, and information with regard to them must be sought elsewhere.[2]

Another useful constant is "P," the period of half-change, or the time taken for the mass of the radioactive substance to be reduced to half its initial value. From the equation given above this is found to bear a constant relation to "λ," that is

$$P = \frac{0 \cdot 6930}{\lambda}.$$

A radioactive element is sometimes distinguished by its "average life" "L," which is simply the reciprocal of the constant "λ," and might be regarded as the average expectation of life of the atoms of the element. It equals $1 \cdot 443 P$.

The Radioactivity of Radium.—The element radium gives out α-[3] and β-rays.[4] The range of the α-rays by the ionisation method is 3·52 cm. at 760 mm. and 15° C.[5,6] The scintillation method gives a somewhat lower value, 3·30 cm.[7] The initial velocity of the α-rays is

[1] Soddy, *Ann. Rep. Chem. Soc.*, 1912, 9, 298; Rutherford, *Phil. Mag.*, 1914, [6], 28, 305.
[2] Rutherford, *Radioactive Substances and their Transformations* (Cambridge University Press), 1913; Curie, *Traité de Radioactivité* (Gauthier-Villars), 1910; see also Rutherford, *Phil. Trans.*, 1904, 204A, 169; Stark, *Jahrb. Radioakt. Elektron.*, 1904, 1, 1; Gruner, *Arch. Sci. phys. nat.*, 1907, [4], 23, 5, 113, 329; Debierne, *Ann. Physique*, 1916, [9], 4, 309.
[3] Rutherford, *Phil. Mag.*, 1905, [6], 10, 193.
[4] Hahn and Meitner, *Physikal. Zeitsch.*, 1909, 10, 741; Baeyer, Hahn, and Meitner, *ibid.*, 1911, 12, 1099; Kolowrat, *Le Radium*, 1910, 7, 269.
[5] Bragg and Kleeman, *Phil. Mag.*, 1904, [6], 8, 726; 1905, 10, 318.
[6] Meyer, *Jahrb. Radioakt. Elektron.*, 1920, 17, 80.
[7] Geiger and Nuttall, *Phil. Mag.*, 1911, [6], 22, 613.

1.53×10^9 cm. per sec.[1,2,3] Radium, apart from its disintegration products, gives 3.57×10^{10} α-particles per sec. per gram of radium,[4,5,6] but in equilibrium with its disintegration products of short life (see later) 14.3×10^{10}.

The heating effect of radium alone is 25.1 cal. per gram per hour.[1,4,6,7] The period of half-change of radium has been estimated by its rate of growth from ionium,[8] and also by counting the number of α-particles given by radium.[4,6,9,10] The International Committee on Chemical Elements for 1923 adopted the value 1690 years.[11]

The yearly production of helium per gram of radium, in equilibrium with its disintegration products of short life, is 164 cub. mm.[4,6,12]

Radioactive Equilibrium.—In radium compounds which have been left untouched for a certain time, there is not only radium but a number of its radioactive disintegration products formed by consecutive changes, as instanced above. These, along with their constants and radiations, are given in the accompanying table : [13]

Element	Atomic Weight.	Period.	λ	Radiation.	Range of α-Ray in Air at 15° C.
			(sec.)$^{-1}$		cm.
Radium . . .	226	1690 years	1.3×10^{-11}	α, β, γ	3 52
Radium emanation . (Niton or Radon)	222	3 85 days	2.085×10^{-6}	α	4·16
Radium A . .	218	3 0 mm.	3.85×10^{-3}	α	4 75
Radium B . .	214	26.8 mm.	4.30×10^{-4}	β, γ	..
Radium C . .	214	19 5 min.	5.92×10^{-4}	α, β, γ	3 80
Radium C′ . .	214	approx. 10^{-6} sec.	approx 10^{-6}	α	6 94
Radium C″← .	210	1·4 min.	8.3×10^{-3}	β, γ	..
Radium D . (Radiolead)	210	16·5 years	1.33×10^{-9}	β, γ	..
Radium E . .	210	5 0 days	1.61×10^{-6}	β, γ	..
Radium F (Polonium)	210	136 days	5.9×10^{-8}	α, γ	3·83
Radium G . . (Uranium lead)	206	Inactive	..	..	..

[1] Meyer, *Jahrb. Radioakt. Elektron.*, 1920, **17**, 80.
[2] Geiger and Nuttall, *loc. cit.*, gave a higher value.
[3] Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, [2a], 1419.
[4] Rutherford, *Phil. Mag.*, 1914, [6], **28**, 320.
[5] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, **81A**, 141; *Physikal. Zeitsch* , 1909, **10**,1,46.
[6] Geiger and Werner found 3.40×10^{10} α-particles per sec., a heating effect of 22·25 cal. per hour per gram, a period of half-change of 1730 years, and a yearly production of helium of 159 cub. mm. per gram, *Zeitsch. Physik*, 1924, **21**, 187.
[7] Rutherford and Robinson, *Phil. Mag.*, 1913, **25**, 312.
[8] Boltwood, *Amer. J. Sci.*, 1908, **25**, 493 , Gleditsch, *ibid.*, 1916, **41**, 112.
[9] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, **81A**, 173 ; Meyer, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, [2a], 1085.
[10] Hess and Lawson, *Arch. Sci.*, 1918, **46**, 330 ; see *Sci. Abs.*, 1919, [A], **22**, 116, No. 306. They obtained 1580 years for the period of half-change by counting α-particles, obtaining $3.72 \pm 0.02 \times 10^{10}$ per sec. per gram for radium alone, a higher number than that found by earlier investigators. The initial velocity deduced from this is 1.59×10^9 cm. per sec. and the range at 15° C. 3·52 cm.
[11] *J. Amer. Chem. Soc.*, 1923, **45**, 867.
[12] Boltwood and Rutherford, *Phil. Mag.*, 1911, [6], **22**, 586.
[13] See also Table of Constants at the end of the chapter.

It will be observed that, compared with that of its disintegration products, the period of radium is very long. The radioactivity of radium, studied over periods of time possible in a lifetime, will appear constant. It will therefore seem to be producing its first disintegration product, radium emanation, at a constant rate. If it be deprived of the emanation present at any moment, fresh emanation will be formed, the quantity increasing until equilibrium is reached, and the rate at which it is formed is equal to the rate at which it is destroyed. The more rapidly it disintegrates, the more rapidly will this point be attained and the smaller will be the number of atoms in radioactive equilibrium. The emanation that was initially present will disappear at a rate fixed by the constant "λ," and at any moment the sum of the separated emanation and that freshly formed by the radium will be the same as the equilibrium quantity.

The rate at which emanation atoms are formed will naturally be the rate at which radium atoms are destroyed, so that if "λ_1" and "λ_2" be the disintegration constants for radium and emanation respectively, and "R" and "E" the number of atoms in equilibrium with one another, $\lambda_1 R = \lambda_2 E$ to a high degree of approximation. That is, the number of atoms of the two radioactive substances, the comparatively long-lived radium and its short-lived emanation in equilibrium, will be inversely proportional to the respective rates of change. Considering also the successive products, radium A, B, C, etc., the same kind of relationship will exist, namely,

$$\lambda_1 R = \lambda_2 E = \lambda_3 A = \lambda_4 B, \text{ etc.}^1$$

In a radioactive series the following relationship is found to hold between the constant of an α-ray producing product and the range of the α-particle :—

$$\log \lambda = Na + 2/3N \log R.$$

where "R" is the range, "a" approximately a constant, and "N" has different values for the different disintegration series, 81 for uranium-radium, 77 for thorium, and 71 for actinium.[2]

THE DISINTEGRATION PRODUCTS OF RADIUM.

Radium Emanation, Radon or Niton.—One of the most interesting of the radioactive derivatives of radium is a gas which closely resembles in chemical inertness the gases of the argon family,[3] Group O of the Periodic Table. Its existence was first recognised by Dorn.[4] Similar gases are also found in the thorium and actinium series, and before the true nature of these substances was fully realised, they were described as emanations. The names *niton* [5] and *radon* [6] have since been given to radium emanation to indicate its relation to the argon group.

[1] Mitchell, *Phil. Mag.*, 1911, [6], 21, 40 ; Lotka, *ibid.*, 1911, [6], 22, 353.

[2] Meyer, Hess, and Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1914, 123, [2a], 1459 ; Meyer, *ibid.*, 1916, 125, [2a], 201 ; Kirsch, *Physikal. Zeitsch.*, 1920, 21, 452 ; see also Geiger and Nuttall, *Phil. Mag.*, 1911, [6], 22, 613.

[3] Ramsay, *B.A. Reports*, 1908, p. 601.

[4] Dorn, *Abh. d. Naturforsch. Ges. für Halle-a.-S.*, 1900.

[5] Ramsay and Gray, *Compt. rend.*, 1910, 151, 126.

[6] See Report of the International Committee on the Chemical Elements for 1923, *J. Amer. Chem. Soc.*, 1923, 45, 867.

As the immediate successor of radium, it must be given off by all radium-containing minerals, and is, probably, mainly responsible, either directly, or indirectly through its products of change, for atmospheric radioactivity.[1] Radium emanation is also found in solution in sea-water,[2] in spring waters,[3] and in sediments.[4] It is to this no doubt that spring waters owe some of their medicinal value.

The physical constants and physical properties of radium emanation have been very carefully studied. It is a colourless gas, but when in highly concentrated form, or condensed, it is brightly luminous, especially at very low temperatures,[5] hence the name *niton*, " the shining one." [6]

As it is derived from radium by an α-ray change, its position in Group O is justified by the displacement law. Further, its atomic weight should be $226 - 4 = 222$. Besides the theoretical evidence just indicated, there is considerable experimental support for this value. Early experiments on the diffusion of the emanation into air or other gases,[7] and in water,[8] or diffusion through a porous solid,[9] gave values which were much too low, although Perkins,[10] by comparing the rates of diffusion of mercury vapour and emanation, found 234 for the atomic weight of the latter. Debierne, however, by an application of Bunsen's effusion method, in which the rate of escape of a gas through a small hole from one low pressure to another still lower is determined, obtained a value 221 with a possible variation of about 2 per cent.[11] Determinations of the density have also been made by weighing by means of the microbalance. The value 223 has thus been found for the atomic weight as the mean of five results varying between 218 and 227.[12]

The value generally accepted for the period of half-change is 3·85 days.[13] According to a recent determination the value is 3·810 days.[14]

The emanation gives off α-rays, and the range of these in air at 15° C.

[1] Elster and Geitel, *Physikal. Zeitsch.*, 1903, 4, 522; Eve, *Phil. Mag.*, 1906, [6], 12, 189; 1907, [6], 14, 724; 1908, [6], 16, 622; Blanc, *ibid.*, 1907, [6], 13, 378; Smyth, *ibid.*, 1912, [6], 24, 632; Satterly, *ibid.*, 1908, [6], 16, 584; *Proc. Cambridge Phil. Soc.*, 1911, 16, 336; Ashman, *Amer. J. Sci.*, 1908, [4], 26, 119; Gockel, *Physikal. Zeitsch.*, 1904, 5, 591; 1908, 9, 304; Mache and Rimmer, *ibid.*, 1906, 7, 617; Hess and Schmidt, *ibid.*, 1918, 19, 109; Olujić, *Jahrb. Radioakt. Elektron.*, 1918, 15, 158.

[2] Knoche, *Physikal. Zeitsch.*, 1912, 13, 112, 152.

[3] Bumstead and Wheeler, *Amer. J. Sci.*, 1904, [4], 17, 97; Berndt, *Ann. Physik*, 1912, [4], 38, 958; Gremacher, *Physikal. Zeitsch.*, 1912, 13, 435; Ramsey, *Phys. Review*, 1916, 7, 284; Krüse, *Jahrb. Radioakt. Elektron.*, 1917, 14, 352.

[4] Gehlhoff, *Physikal. Zeitsch.*, 1906, 7, 590.

[5] Rutherford, *Phil. Mag.*, 1909, [6], 17, 723.

[6] Ramsay and Gray, *Compt. rend.*, 1910, 151, 126.

[7] Rutherford and Brooks, *Trans. Roy. Soc. Canada*, 1901, 7, Section III, 21; *Chem. News*, 1902, 85, 196; Curie and Danne, *Compt. rend.*, 1903, 136, 1314; Chaumont, *Le Radium*, 1909, 6, 106.

[8] Wallstabe, *Physikal. Zeitsch.*, 1903, 4, 721.

[9] Bumstead and Wheeler, *Amer. J. Sci.*, 1904, [4], 17, 97; Makower, *Phil. Mag.*, 1905, [6], 9, 56.

[10] Perkins, *Amer. J. Sci.*, 1908, [4], 25, 461.

[11] Debierne, *Compt. rend.*, 1910, 150, 1740; *Ann. Physique*, 1915, [9], 3, 62.

[12] Gray and Ramsay, *Proc. Roy. Soc.*, 1911, [A], 84, 536; *Compt. rend.*, 1910, 151, 126; *Ann. Chim. Phys.*, 1910, [8], 21, 145, 574; *Jahrb. Radioakt. Elektron.*, 1911, 8, 5.

[13] Mme. Curie, *Le Radium*, 1910, 7, 33; Rutherford, *Sitzungsber. K. Akad. Wiss. Wien*, 1911, 120, 303; see also Rutherford and Soddy, *Phil. Mag.*, 1903, [6], 5, 445; Rümelin, *ibid.*, 1907, [6], 14, 550; *Physikal. Zeitsch.*, 1907, 8, 803; Sackur, *Ber.*, 1905, 38, 1753; Bumstead and Wheeler, *loc. cit.*

[14] Bothe and Lechner, *Zeitsch. Physik*, 1921, 5, 335.

is 4·16 cm. or 3·94 cm. at 0° C. and atmospheric pressure.[1]   The production of helium by radium emanation was proved by Ramsay and Soddy.[2]

A number of observations have been made on the spectrum of radium excited by the electric discharge at low pressures.[3]   Nyswander, Lind, and Moore[4] have made both photographic and visual measurements of the spectrum from λ 3982 to 7450 Å., and find that, in many cases, the intensities differ markedly from those found by previous observers. The intensity apparently changes, however, with duration of discharge, some lines decreasing and some increasing in strength, whilst the colour of the discharge also varies.   In addition, several new lines were found. Some of the strongest lines observed photographically, and also obtained by other investigators, are : 7054·0, 4721·2, 4609·2, 4577·6, 4508·5, 4459·4, 4435·1, 4349·5, 4307·9, 4166·9, 3981·8 Å. The following lines were observed visually : 5483, 5058, 4826, 4735 Å.

The emanation condenses to a liquid at low temperatures.   Its behaviour is strictly comparable with that of ordinary gases, since different vapour pressures are obtained at different temperatures, as shown by the following table[5] :—

Pressure, mm. .	.	760	250	50	9
Temperature, °C.	.	−65	−78	−101	−127

The boiling-point under ordinary atmospheric pressure is thus −65° C.[6]   The critical temperature is 104·5° C., and the pressure 62·4 atmospheres.[6]   The freezing-point is −71° C., and the vapour pressure at this temperature is 500 mm.[6]   The density of liquid emanation is 5–6.[5, 6]

The emanation is slightly soluble in water, the absorption coefficient, or the ratio of the amount of emanation dissolved in a given volume of water to the amount present in an equal volume of air in equilibrium with it, at 18° C., being 0·285.   It diminishes with rise of temperature from 0·52 at 0° C. to 0·108 at 91° C.[7, 8]   It is less soluble in salt solutions than in pure water ;[8, 9] in sea water, for instance, the coefficient is 0·255 at 14° C.[8]   It is, however, much more soluble in many organic liquids, among others the following values for the coefficient of absorption have been obtained at 18° C. : absolute alcohol, 6·17 ; benzene, 12·82 ; ether, 15·08 ; carbon disulphide, 23·14.[10, 11]   Dolezalek's theory, connecting vapour pressure with solubility,[12] appears to apply.[11]

[1] Rutherford, *Radioactive Substances and their Radiations* (Cambridge University Press), 1913, p. 164.

[2] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, [A], **72**, 204 ; 1904, [A], **73**, 346 ; see Himstedt and Meyer, *Ann. Physik*, 1904, [4], **15**, 184 ; 1905, [4], **17**, 1005.

[3] Ramsay and Collie, *Proc. Roy. Soc.*, 1904, [A], **73**, 470 ; Cameron and Ramsay, *ibid.* 1908, [A], **81**, 210 ; Rutherford and Royds, *Phil. Mag.*, 1908, [6], **16**, 313 ; Royds, *ibid.* 1909, [6], **17**, 202 ; *Proc. Roy. Soc.*, 1909, [A], **82**, 22 ; Watson, *ibid.*, 1910, [A], **83**, 50.

[4] Nyswander, Lind, and Moore, *Astrophys. J.*, 1921, **54**, 285 ; see also *Phys. Review*, 1920, **15**, 239.

[5] Rutherford, *Phil. Mag.*, 1909, [6], **17**, 723.

[6] See also Gray and Ramsay, *Trans. Chem. Soc.*, 1909, **95**, 1073.

[7] Ramstedt, *Le Radium*, 1911, 8, 253 ; Kofler, *Monatsh.*, 1913, **34**, 389 ; see also von Traubenberg, *Physikal. Zeitsch.*, 1904, **5**, 130 ; Hofmann, *ibid.*, 1905, 6, 337 ; Mache, *Sitzungsber. K. Akad. Wiss. Wien*, 1904, **113**, 1329 ; Meyer, *ibid.*, 1913, **122**, [2a], 1281, see *Sci. Abs.*, 1914, [A], **17**, 199.

[8] Boyle, *Phil. Mag.*, 1911, [6], **22**, 840.

[9] Kofler, *Physikal. Zeitsch.*, 1908, 9, 6 ; *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, 1473.

[10] Ramstedt, *loc. cit.* ; see also Boyle, *loc. cit.* ; Szeparowicz, *Sitzungsber. K. Akad. Wiss. Wien*, 1920. **129**, [2a], 437.

[11] Swinne, *Zeitsch. physikal. Chem.*, 1913, **84**, 348 ; Schulze, *ibid.*, 1920, **95**, 257.

[12] Dolezalek, *ibid.*, 1908, **64**, 727 ; 1910, **71**, 191.

By observations on the rate of diffusion of the emanation through water [1] and other liquids,[2] a value for the atomic diameter of the order of 1.85×10^{-8} cm. has been found.

Radium emanation is strongly occluded by some solids, for example, rubber and celluloid,[3] and especially by charcoal, preferably cocoanut charcoal.[4] Solid radium salts and minerals also occlude the greater part of the emanation,[5] so that for the separation and purification of the gas it is best to dissolve the radium preparation in water. The emanation may then be pumped or boiled off, dried by phosphorus pentoxide, the gases thus obtained exploded to remove the hydrogen and oxygen always contained in them, carbon dioxide removed by potassium hydroxide, and the final residue, usually consisting chiefly of emanation, hydrogen, and helium, cooled by liquid air, which causes the emanation to condense so that the remaining gases may be removed by the pump. Further purification may be effected by successive condensations.[6] Separation by adsorption in colloidal silicic acid has been suggested.[7]

Radium emanation, in common with other radiating substances, has a strong influence on chemical reactions. For example, it brings about the decomposition of ammonia [8] and hydrogen sulphide,[9] the combination of hydrogen and oxygen with the formation of hydrogen peroxide and water,[10] the reduction of carbon monoxide by hydrogen,[11] and so on.

Minute quantities are best determined by dissolving in water or acid the substance to be examined, or fusing it with alkali carbonate and bisulphate, drawing off the emanation thus set free into an evacuated vessel, and measuring its activity. Care must be taken that the solution does not deposit any trace of solid which might tend to occlude the emanation and so give too low a result.[12]

Taking into account the number of α-particles emitted by radium itself, the calculated amount of emanation in equilibrium with 1 grm. of radium is 0.59 cub. mm. Experimental values in very close agreement with this have been found by different investigators.[13] The Radiology Congress at Brussels in 1910 decided to make this equilibrium quantity of emanation a unit, and called it the " curie." A more convenient unit is the " millicurie," or the amount of emanation in equilibrium with 1 mgm. of radium. In the determination of the emanation

[1] Ramstedt, *Medd. K. Vetenskapsakad Nobel-Inst.*, 1919, 5, No. 5, 1.

[2] Róna, *Zeitsch. physikal. Chem.*, 1917, 92, 213.

[3] Curie and Danne, *Compt. rend.*, 1903, 136, 364.

[4] Rutherford, *Nature*, 1906, 74, 634 ; Boyle, *Phil. Mag.*, 1909, [6], 17, 374 ; Satterly, *ibid.*, 1910, [6], 20, 778.

[5] Kolowrat, *Le Radium*, 1910, 7, 266.

[6] Rutherford, *Phil. Mag.*, 1908, [6], 16, 300.

[7] Ebler, *J. Chem. Soc.*, 1914, 106, Abs. ii, 410.

[8] Usher, *Trans Chem. Soc*, 1910, 97, 389, 1193 ; Wourtzel, *Compt. rend.*, 1914, 158, 571.

[9] Wourtzel, *ibid.*, 1913, 157, 929.

[10] Scheuer, *ibid.*, 1914, 159, 423.

[11] Scheuer, *ibid.*, 1914, 158, 1887.

[12] Rutherford and Boltwood, *Amer. J. Sci.*, 1905, 20, 55 ; 1906, 22, 1 ; Eve, *ibid.*, 4 ; Mme. Curie, *Le Radium*, 1910, 7, 65 ; Duane and Laborde, *Compt. rend.*, 1910, 150, 1421 ; Lind, *J. Ind. Eng. Chem.*, 1915, 7, 1024 ; Moran, *Trans. Roy. Soc. Canada*, 1916, 10, Section III, 57 ; Underwood and Schlundt, *Trans. Amer. Elektrochem. Soc.*, 1918, 34, 203.

[13] Rutherford, *Phil. Mag*, 1908, [6], 16, 300 ; Gray and Ramsay, *Trans Chem. Soc.*, 1909, 95, 1073 ; Debierne, *Compt. rend.*, 1909, 148, 1264 ; *Ann. Physique*, 1915, [9], 3, 18.

content of natural waters a still smaller unit, the millimicrocurie, is employed.[1]

For medical purposes it is often found more convenient to use a closed capsule of emanation rather than the original radium salt.

Radium Active Deposit of Short Life.—M. and Mme. Curie first noticed that inactive bodies left in the immediate neighbourhood of radium compounds acquired a temporary radioactivity, which was gradually lost on removal of the radium.[2] This was at first known as induced activity.

A similar phenomenon was observed also in the case of thorium,[3] and at the same time it was shown that the activity is really due to the formation of a thin film of radioactive matter, the disintegration product of the emanation, on the surface of the inactive body. When an emanating substance is placed inside a closed vessel the whole interior surface of the vessel becomes coated with active deposit, although the amount present in different parts is, to some extent, influenced by gravity.[4] However, in a strong electric field the activity is confined largely to the negative electrode,[5] indicating that it is charged positively. A certain proportion, nevertheless, goes to the anode, and this is usually explained by the supposition that the positive charge of the active deposit is neutralised by negative ions in the ionised gas, and it then reaches the anode by diffusion, or, that it may even become negatively charged.[6] The particles of active deposit, especially when concentrated, may also tend to form, with the ions in the gas, large aggregates which do not diffuse to the walls but remain in the gas.[7] It is uncertain whether the deposit is charged on formation or acquires its charge later, and the possibility of an initial negative charge is not excluded.[8]

In ethyl ether the active deposit appears to be neutral and to reach the electrodes by diffusion alone.[9] A similar result is obtained in ethyl bromide, but in dry air, hydrogen, oxygen, and carbon dioxide it is negatively charged.[10]

It has been shown, however, that the electric wind has an important effect on the results obtained.[11] If the electrodes consist of a sharp needle-point opposite a disc and high potentials are employed, the electric wind drives the deposit to the disc independently of whether it is positively or negatively charged. The active deposit has also the property of spreading a little to surrounding surfaces after deposition, as if slightly volatile.[12]

At pressures below 10 mm. of mercury the activity of the cathode

[1] See under Water, Vol. VII. of this series, Part I.
[2] Curie and Mme. Curie, *Compt. rend.*, 1899, 129, 714.
[3] Rutherford, *Phil. Mag.*, 1900, [5], 49, 161.
[4] Mme. Curie, *Compt. rend.*, 1907, 145, 477.
[5] Rutherford, *Phil. Mag.*, 1900, [5], 49, 161.
[6] Schmidt, *Physikal. Zeitsch.*, 1908, 9, 184; Eckmann, *Jahrb. Radioakt. Elektron.*, 1912, 9, 157; Wellisch and Bronson, *Phys. Review*, 1912, 34, 151; *Phil. Mag.*, 1912, [6], 23, 714; Walmsley, *ibid.*, 1914, [6], 28, 539.
[7] Debierne, *Ann. Physique*, 1915, [9], 4, 27.
[8] Wertenstein, *Compt. rend.*, 1915, 161, 696.
[9] Wellisch, *Phil. Mag.*, 1914, [6], 28, 417; *Amer. J. Sci.*, 1913, [4], 36, 315; 1914, [4], 38, 283.
[10] Henderson, *Trans. Roy. Soc. Canada*, 1917, [3], 10, 151.
[11] Ratner, *Phil. Mag.*, 1917, [6], 34, 429.
[12] Ratner, *ibid.*, 1918, [6], 36, 397.

steadily diminishes with pressure,[1] and the deposit is distributed instead over the interior surface of the vessel.[2] This is due to the recoil of the active deposit.[3] When an atom of emanation breaks up with the emission of an α-particle travelling at a high velocity, the residue of the atom which forms the active deposit acquires an equal and opposite momentum, and recoils with a considerably less velocity, owing to its much greater mass. Whilst recoiling, the electric field has no influence on it, but when it is brought to rest by collision, after travelling a very short distance in air at ordinary pressures, it can then be directed to the cathode. At low pressures the recoil atoms travel much further before being stopped, and thus reach the walls of the vessel where they remain.

When the active deposit is removed from the emanation, the activity, as measured by the α-rays, rapidly disappears. If it consisted of a single radioactive product disintegrating to an inactive substance, or to one giving β-rays only, its rate of disappearance would follow a simple exponential law, and would be independent of the length of the time of exposure to the emanation. This is not so however.[4] The form of the decay curve varies with the time of exposure, provided this is under four hours, and does not follow an exponential law until several hours after removal from the emanation.[5]

Rutherford showed that the decay curves for different types of radiation could be explained by the assumption that there are three products formed successively in the active deposit: radium A, with a period of about 3 minutes and emitting only α-rays; radium B, then thought to be rayless and to have a period of 21 minutes; and radium C, emitting α-, β-, and γ-rays and probably with a period of 28 minutes.[6]

Radium Active Deposit of Long Life.—The active deposit formed on a surface after a comparatively short exposure to radium emanation appears to be lost rapidly and completely. After a very long exposure, on the other hand, the surface retains a small residual activity, the magnitude of which depends on the quantity of emanation and on the time of exposure to it.[7]

This residual activity, as measured by its α-radiation, was found to increase with time, showing signs, after 300 days, of approaching a maximum. The β-ray activity also increased, reaching a maximum after 40 days, when it became practically constant. Further study showed that the changes observed might be explained by postulating the existence of three products: radium D, formed from radium C, of period about 16 years and emitting β-rays; radium E, also a β-ray product and with a period of approximately 5 days; and radium F, an α-ray product, with a period of about 140 days and apparently identical with the polonium found by Mme. Curie in pitchblende.

[1] Makower, *Phil. Mag.*, 1905, [6], 10, 526; Jackson, *ibid.*, 532; Russ, *ibid.*, 1908, [6], 15, 601.

[2] Hahn and Meitner, *Ber. Deut. physikal. Ges.*, 1909, 11, 55.

[3] See Hahn, *Jahrb. Radioakt. Elektron.*, 1910, 7, 296, a bibliography is given; Wertenstein, *Ann. Physique*, 1914, [9], 1, 347.

[4] Rutherford and Brooks, *Phil. Mag.*, 1902, [6], 4, 1.

[5] Curie and Danne, *Compt. rend.*, 1903, 136, 364.

[6] Rutherford, *Phil. Trans.*, 1904, 204A, 169; see also Curie and Danne, *Compt. rend.*, 1904, 138, 683; Schmidt, *Jahrb. Radioakt. Elektron.*, 1907, 4, 195.

[7] Mme. Curie, *Thèse présentée a la Faculté des Sciences de Paris*, 1903, English translation reprinted from *Chem. News*, 1904, p. 79; Rutherford, *Phil. Trans.*, 1904, 204A, 169; *Phil. Mag.*, 1904, [6], 8, 636; 1905, [6], 10, 290.

PREPARATION AND PROPERTIES OF THE SOLID DISINTEGRATION PRODUCTS OF RADIUM.

Radium A.—Radium A is formed from radium by two successive α-ray changes. It therefore has an approximate atomic weight of $226 - 2 \times 4 = 218$. For reasons which will be discussed later, it may be regarded as an element in the sixth group of the Periodic Table. Its period of half-change is 3·05 minutes,[1] and it emits α-rays of range 4·75 cm. in air at 15° C.,[1, 2] and of initial velocity 1.69×10^9 cm. per sec.[3] Owing to its very short life the amount in equilibrium with 1 grm. of radium is exceedingly small, 3.54×10^{-9} grm. It is not to be expected, therefore, that its presence can ever be detected otherwise than by its radioactive properties.

The heat given out by the radium A in equilibrium with 1 grm. of radium is 30·5 cal. per hour.[4]

Radium A is volatile in hydrogen below 650° C.,[5] but in air only at 800°–900° C.,[6] probably indicating in the latter case the formation of a less volatile oxide.

When radium emanation is dissolved in pure water the active deposit is obtained either suspended or dissolved in the water. On putting in two electrodes, with a potential difference of about 200 volts between them, radium A is found to travel to the anode. It is therefore regarded as a negative hydrosol.[7] The introduction of a small amount of hydrogen ions through the addition of acid coagulates the hydrosol and reduces the concentration at the anode. Polyvalent cations, such as aluminium, produce a similar effect. With larger quantities of acid, above $\frac{10}{17} N$ for example, radium A is deposited at the cathode. Possibly electrolytic conduction takes the place of cataphoresis. With the addition of a small amount of hydroxyl ion the stability of the hydrosol is increased at first, and therefore the activity at the anode increases, but decreases again above a concentration of $\frac{0.4}{17} N$ base. The citrate ion produces a similar but more pronounced effect. On dipping filter-paper into the aqueous solution radium A rises on the filter-paper, indicating a negative charge, and on filtering it passes through the filter-paper.[8] The solvent has a considerable effect on the charge of the colloid. In alcohol, radium A goes to the cathode.[9]

Radium A is soluble in organic solvents, especially in carbon disulphide, which is in agreement with its position in the sulphur group.[10] When deposited on plates of gold or platinum electrolytically saturated with hydrogen the solubility is diminished.[10]

By precipitation in the presence of different metals, radium A is shown to bear a resemblance to mercury, bismuth, and tellurium. It can be separated from mercury, however, by precipitation with bismuth

[1] See Meyer, "Radioactive Constants in 1920," *Jahrb. Radioakt. Elektron.*, 1920, 17, 80.
[2] Bragg and Kleeman, *Phil. Mag.*, 1905, [6], 10, 318, found 4·83±0 05 cm.
[3] Tunstall and Makower, *ibid.*, 1915, [6], 29, 259.
[4] Rutherford and Robinson, *ibid.*, 1913, 25, 312.
[5] Russell, *Proc. Roy. Soc.*, 1911, 86A, 240 ; *Phil. Mag.*, 1912, [6], 24, 134.
[6] Makower, *Le Radium*, 1909, 6, 50 ; Ramsauer, *ibid.*, 1914–1919, 11, 100 ; see also Duane, *J. Physique*, 1905, 4, 618.
[7] Godlewski, *Le Radium*, 1913, 10, 250.
[8] Godlewski, *Kolloid. Zeitsch.*, 1914, 14, 229 ; *Le Radium*, 1914–1919, 11, 161.
[9] Lachs, *Kolloid. Zeitsch.*, 1917, 21, 165.
[10] Ramstedt, *Le Radium*, 1913, 10, 159.

phosphate, and from bismuth by precipitation with metallic tellurium. It evidently has most affinity with the tellurium group.[1]

Radium B.—Since radium B is formed from radium A with the emission of an α-particle, its atomic weight should be approximately 214. Its position in the Periodic Table is in the fourth or carbon group.[2] Its period of half-change is 26·8 minutes,[3] and it gives β-rays[4] and γ-rays.[5] The amount in equilibrium with 1 grm. of radium should be $3·05 \times 10^{-8}$ grm., and the heating effect of this quantity is at most 2 per cent. of that of the radium C in equilibrium with it.[6]

Radium B can be separated in a pure state from radium A by the recoil method. An inactive negatively charged plate is placed near a plate covered with radium A, and radium B is obtained on the former.[7] The range of the recoil atoms of radium B in air is about 0·14 mm. at atmospheric pressure, and 0·83 mm. in hydrogen,[8] ionisation taking place as with the α-rays.[9] The ionisation tracks can be photographed.[10] The behaviour of the recoil atoms in an electric and magnetic field *in vacuo* indicates that they carry a single positive charge,[11] and they bring about chemical reaction in the same way as α-rays, for example, the union of hydrogen and oxygen.[12]

Radium B may be completely volatilised at about 650° C. in hydrogen, but not below 700° C. in oxygen, apparently indicating the formation of an oxide in the latter case.[13]

In pure water radium B apparently forms a positive hydrosol and is stabilised by hydrogen ions and polyvalent cations.[14] It is adsorbed by negative sols, such as arsenious sulphide, and colloidal platinum and gold, and when filtered it is retained by the filter-paper.[14] Lachs and Herszfinkel stated that this action could be explained by supposing radium B present in the ionic state.[15]

In alcohol it is mainly deposited on the anode.[16]

Radium B dissolves very readily in dilute acids, more quickly than radium C or A when deposited on platinum or gold plates saturated with hydrogen, and more quickly than radium C from plates saturated

[1] Beer, *Le Radium*, 1914–1919, **11**, 124.

[2] Fajans, *ibid.*, 1913, **10**, 61.

[3] Bronson, *Phil. Mag.*, 1906, [6], **11**, 143 ; von Lerch, *Ann. Physik*, 1906, **20**, 345 ; Mme. Curie, *Traité de Radioactivité* (Gauthier-Villars), 1910, vol. ii, p. 322.

[4] Baeyer, Hahn, and Meitner, *Physikal. Zeitsch.*, 1911, **12**, 1099 ; Schmidt, *Ann. Physik*, 1906, **21**, 609 ; Fajans and Makower, *Phil. Mag.*, 1912, [6], **23**, 296 ; Rutherford and Robinson, *ibid.*, 1913, **26**, 717 ; Chadwick, *Ber. Deut. physikal. Ges.*, 1914, **16**, 383 ; Danysz, *Le Radium*, 1913, **10**, 4.

[5] Moseley and Makower, *Phil. Mag.*, 1912, [6], **23**, 302; Rutherford and Andrade, *ibid.*, 1914, [6], **27**, 854 ; **28**, 263 ; Kohlrausch, *Jahrb. Radioakt. Elektron.*, 1918, **15**, 64.

[6] Herszfinkel and Wertenstein, *J. Physique et Le Radium*, 1920, **1**, 143.

[7] Russ and Makower, *Proc. Roy. Soc.*, 1909, **82A**, 205 ; see also Brooks, *Nature*, 1904, **70**, 270.

[8] Wertenstein, *Compt. rend.*, 1910, **150**, 869 ; *Ann. Physique*, 1914, [9], **1**, 388.

[9] Wertenstein, *Compt. rend.*, 1911, **152**, 1657 ; *Le Radium*, 1912, **9**, 6.

[10] Bose and Ghosh, *Phil. Mag.*, 1923, [6], **45**, 1050.

[11] Walmsley and Makower, *ibid.*, 1915, [6], **29**, 253 ; Russ and Makower, *ibid.*, 1910, [6], **20**, 875 ; Makower and Evans, *ibid.*, 882.

[12] Lind, *J. Amer. Chem. Soc.*, 1919, **41**, 551.

[13] Russell, *Phil. Mag.*, 1912, [6], **24**, 134 ; see also Curie and Danne, *Compt. rend.*, 1904, **138**, 748 ; Bronson, *Amer. J. Sci.*, 1905, **20**, 60 ; *Phil. Mag.*, 1906, [6], **11**, 143 ; Loria, *Monatsh.*, 1916, **37**, 173 ; Ramsauer, *Le Radium*, 1914–1919, **11**, 100 ; but see Makower, *ibid.*, 1909, **6**, 50.

[14] Godlewski, see Radium A.

[15] Lachs and Herszfinkel, *J. Physique et Le Radium*, 1921, **2**, 319.

[16] Lachs, see Radium A.

with oxygen when the oxides of the active deposit are probably formed. Oxygen, however, diminishes the solubility of both B and C.[1] Radium B dissolves less readily than radium C in alkaline solutions and sodium carbonate. It is also not very soluble in organic liquids.

The valency of radium B, as determined by diffusion, is 2.[2]

The chemical properties of radium B are the same as those of lead,[3] and the electrolytic potentials of the two are the same to an accuracy of 2×10^{-5} volt, which is one hundred times less than the differences observed in the same metal.[4]

Radium C.—Radium C was at first regarded as a simple substance emitting a-, β-, and γ-rays,[5] and of period 19·5 minutes.[5] It is now known to be complex and to exhibit the phenomenon of branching. Hahn and Meitner,[6] on examining the recoil radiations from radium C, found a short-lived product of period about 2 to 2·5 minutes, the activity being very minute compared with that of the radium C from which it had come.

Fajans, after a more detailed examination,[7] stated that the period was 1·38 minutes and that the substance emitted β-rays of about the same penetrating power as those emitted by radium C, but of only approximately $\frac{1}{8000}$ of the activity. It was at first thought that the minuteness of the quantity indicated that it was formed by recoil from a β-ray change.[8] Radium C, however, produced radium D by recoil in an amount to be expected from an a-ray change. It was shown that the new product could not come before radium C,[9] and it was finally suggested that the latter must break up in two ways, the major part, 99·97 per cent., in fact, giving radium D, and the rest the new β-ray product of short period.

Finally, Fajans attributed the production of radium D to a very short-lived product of period of the order of 10^{-6} second, which emits a-rays of range 6·57 cm. at 0° C., or 6·94 at 15° C., and is derived from radium C by a β-ray change.[10] A later determination gives the range as 6·592 cm. at 0° C.[11] The period has not been tested experimentally, but is required by the Geiger-Nuttall relation between range of a-ray and period.[12]

According to the most recent views the changes which radium C undergoes may be represented by the following scheme [13] :—

[1] Ramstedt, Le Radium, 1913, 10, 159.

[2] von Hevesy, Physikal. Zeitsch., 1913, 14, 1202.

[3] See section on Isotopes.

[4] Klemensiewicz, Compt. rend., 1914, 158, 1889.

[5] von Lerch, Ann. Physik, 1906, 20, 345. Study of β-rays by Rutherford and Robinson, Phil. Mag., 1913, [6], 26, 717 ; see also Baeyer, Hahn, and Meitner, Physikal. Zeitsch., 1911, 12, 1099. Study of γ-rays, Rutherford and Andrade, Phil. Mag., 1914, 28, 263 ; Kohlrausch, Jahrb. Radioakt. Elektron., 1918, 15, 64.

[6] Hahn and Meitner, Physikal. Zeitsch., 1909, 10, 697.

[7] Fajans, ibid., 1911, 12, 369 ; see also Fajans and Makower, ibid., 378.

[8] Makower and Russ, Phil. Mag., 1910, [6], 19, 100 ; Proc. Physical Soc., 1910, 22, 147.

[9] Fajans and Makower, Phil. Mag., 1912, [6], 23, 292.

[10] Fajans, Physikal. Zeitsch., 1912, 13, 699 ; 1913, 14, 951.

[11] Henderson, Phil. Mag., 1921, [6], 42, 538.

[12] Geiger and Nuttall, ibid., 1911, 22, 613 ; 1912, 23, 439.

[13] Albrecht, Sitzungsber. K. Akad. Wiss. Wien, 1919, 128, 925 ; see also Russell, An Introduction to the Chemistry of Radioactive Substances (John Murray), 1922, pp. 49, 59. According to earlier nomenclature, RaC=RaC₁, RaC″=RaC₂, and RaC′ remains the same ; see Fajans, Zeitsch. Elektrochem., 1917, 23, 250 ; Meyer and von Schweidler, ibid., 1918, 24, 36 ; Schmidt, Zeitsch. anorg. Chem., 1918, 103, 116.

$$\text{Radium B} \xrightarrow{\beta} \text{Radium C} \begin{cases} \xrightarrow{\alpha} & \begin{matrix} 0\cdot04 \text{ per cent.} \\ \text{Radium C}'' \xrightarrow{\beta} \\ 1\cdot4 \text{ min.} \end{matrix} \\ \xrightarrow{\beta, \gamma} & \begin{matrix} 99\cdot96 \text{ per cent.} \\ \text{Radium C}' \xrightarrow{\alpha} \text{Radium D} \xrightarrow{\beta, \gamma} \\ \text{Approx. } 10^{-6} \text{ sec.} \end{matrix} \end{cases}$$

Radium B   26·8 min.   Radium C   19·5 min.
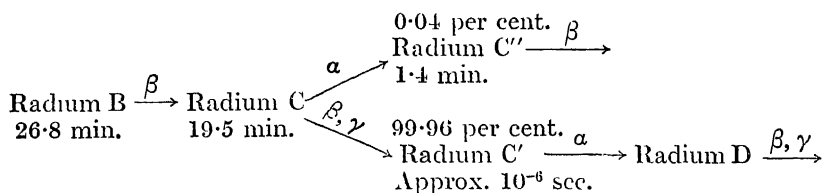
Radium C' has too short a life to be separable from radium C, so that the latter is best detected by the α-radiation of radium C'. Radium C and C', being formed by β-ray changes, should have an atomic weight of 214, the same as radium B, and radium C'', 210.

The initial velocity of the α-rays of radium C' is $1\cdot922 \times 10^9$ cm. per sec.[1]

The heat produced by the amount of radium B and C (including C' and C'') together in equilibrium with 1 grm. of radium is 50·5 cal. per hour.[2]

Radium C is more electropositive than radium B.[3] It is a member of the fifth group of the Periodic Table, and its chemical properties are the same as those of bismuth from which it is chemically inseparable.[4] Diffusion experiments show that radium C is tervalent.[5]

The chemical and physical properties of radium B and C have been studied chiefly from the point of view of the contrasts they may offer to one another, and hence the possibilities of separation, since they are obtained together in the active deposit.

It was soon found that on heating the active deposit, radium B could be volatilised and radium C left behind.[6] Makower studied the volatilisation of radium C by heat from different surfaces. In all cases volatilisation was noticeable between 700° and 800° C. From platinum and nickel it was complete at 1200° C., but from a quartz surface it was incomplete at 1300° C.[7] These high temperatures were probably required because of the formation of an oxide in air, or, in the case of quartz, possibly even a silicate, for Russell found that in hydrogen it volatilised at about 360° ±20° C.[8]

Radium C and C'' can be separated from a solution of the active deposit in hydrochloric acid by dipping into the hot solution a copper or nickel plate upon which they are then deposited.[9] When bismuth is present in the solution only radium C'' is obtained.[10]

Von Hevesy studied the precipitation of radium B and C from a solution of the equilibrium mixture upon single electrodes for different

[1] Albrecht, loc. cit. ; see also Rutherford, Phil. Mag., 1906, [6], 12, 348.

[2] Rutherford and Robinson, Phil. Mag., 1913, [6], 25, 312.

[3] von Lerch, loc. cit. ; von Hevesy, Physikal. Zeitsch., 1912, 13, 672 ; Le Radium, 1913, 10, 65 ; Fajans, ibid., 1913, 10, 57.

[4] Fleck, Trans. Chem. Soc., 1913, 103, 381.

[5] von Hevesy, Physikal. Zeitsch., 1913, 14, 1202.

[6] Curie and Danne, Compt. rend., 1904, 188, 748.

[7] Makower, Le Radium, 1909, 6, 50 ; see also Loria, Monatsh., 1916, 37, 173 ; Ramsauer, Le Radium, 1914–1919, 11, 100.

[8] Russell, Phil. Mag., 1912, [6], 24, 134.

[9] von Lerch, Ann. Physik, 1906, 20, 345 ; see also Meitner, Physikal. Zeitsch., 1911, 12, 1094.

[10] Russell, An Introduction to the Chemistry of the Radioactive Substances (John Murray), 1922, p. 154.

potentials between electrode and solution.[1] The results are given in the following table and plotted on Curve I.

V .	. 0·49	0·43	0·3	0·1	0	−0·1	−0·3	−0·5	−0·6	−0·7	−0·9	−1·1	−1·9
Percentage, RaB .	. 0	1	3	7	10	13	17·5	29	40	64	76	80·5	83

" V " is the electrode potential measured against the calomel electrode as zero. Fifty per cent. radium B represents the proportions in radioactive equilibrium. It is thus seen that on silver in a molar solution of silver nitrate, pure radium C is deposited; on silver in a solution of silver cyanide in potassium cyanide of suitable concentration, equilibrium amounts; and on magnesium in 0·5 molar magnesium sulphate solution, 83 per cent. radium B.

The curve may also be used as a means of determining unknown potential differences.[1]

Radium C may be obtained in colloidal form in neutral solution
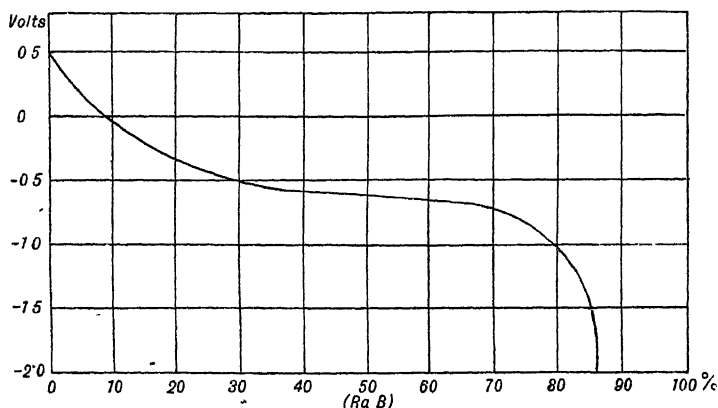
CURVE I.

as a negative hydrosol.[2, 3] It is found, however, at both the cathode and the anode when a potential difference is applied. Godlewski suggested that this was due to the fact that in the α-ray change of radium A, the radium B atom produced is expelled by recoil from the colloidal aggregate and is thus free to travel in accordance with its charge, whereas the radium C atom produced in the β-ray change of radium B is not expelled, but remains in the aggregate and moves to the cathode when an excess of radium B is present.[3] In alcoholic solution radium C goes to the anode only.[4]

The behaviour of a neutral solution of the active deposit when a filter-paper is dipped into it might be utilised for the separation of radium C. Radium B and C are present on the immersed part and also a little above the surface if the immersion is long. The presence of radium B is due to the rising of radium A, which, however, cannot get far owing to its short life, but gives radium B which is at once precipitated. At higher levels is pure radium C.[2]

[1] von Hevesy, *Phil. Mag.*, 1912, [6], **23**, 628.
[2] Godlewski, *Le Radium*, 1914–1919, **11**, 161.
[3] Godlewski, *Phil. Mag.*, 1914, [6], **27**, 618.
[4] Lachs, *Kolloid. Zeitsch.*, 1917, **21**, 165.

The observation that the solubility of radium C in alkaline solution is greater than that of radium B,[1] is in accordance with the view that radium C is a negative colloid. It is not readily soluble in organic liquids.

It is possible to obtain radium C from B by β-ray recoil. Russ and Makower only obtained quantities varying from $\frac{1}{1000}$ to $\frac{1}{500}$ of the theoretical amount,[2] but Muszkat has obtained a yield $\frac{1}{5}$ of the theoretical.[3]

Radium D, or Radiolead.—Radium D is formed from radium C by a β- and a-ray change in succession. Its atomic weight is therefore approximately 210. It belongs to the same group of the Periodic Table as radium B, the fourth group. The two have, in fact, identical properties.[4] Diffusion experiments in solution show that radium D is divalent.[5]

Radium D emits weak β-rays[6] and γ-rays,[7] and has a period of 16 years.[8]

It was early noticed that lead separated from pitchblende possessed a considerable activity which was at first ascribed to the presence of small quantities of radium and polonium.[9] It was shown, however, that it was probably a new radioactive substance to which the name radiolead was given.[10] Later it was found that radium D, the first transformation product in the active deposit of long life, has the same properties as the active constituent of radiolead.[11]

There is a radioactive mineral, *Vesuvian cotunnite*, which contains no radium, but only radium D and its derivatives.[12]

Radium D may be obtained in the pure state by recoil from radium C.[13] It has a range of 100 mm. in air at 1 mm. pressure.[14] In high vacua the recoil atom does not carry a charge,[14] but at atmospheric pressure it has a single positive charge.[11, 15]

[1] Ramstedt, *Le Radium*, 1913, 10, 159.

[2] Russ and Makower, *Phil. Mag.*, 1910, [6], 19, 100; see also Hahn and Meitner, *Ber. Deut. physikal. Ges.*, 1909, 11, 55.

[3] Muszkat, *J. Physique et Le Radium*, 1921, 2, 93.

[1] See section on Isotopes.

[5] von Hevesy, *Physikal. Zeitsch.*, 1913, 14, 1202.

[6] Kovarik, *Phil. Mag.*, 1910, [6], 20, 849; Baeyer, Hahn, and Meitner, *Physikal. Zeitsch.*, 1911, 12, 378, 1099; Danysz, *Compt. rend.*, 1911, 153, 339, 1066; *Le Radium*, 1913, 10, 4; Meitner, *Physikal. Zeitsch.*, 1915, 16, 272.

[7] Rutherford and Richardson, *Phil. Mag.*, 1913, [6], 26, 324.

[8] Meyer and von Schweidler, *Sitzungsber. K. Akad. Wiss. Wien*, 1907, 116, 701; *Physikal. Zeitsch.*, 1907, 8, 457; Curie, *Le Radium*, 1911, 8, 353; Rossi, *Rend. Accad. Lincei*, 1912, 21, 462; Antonoff, *Phil. Mag.*, 1910, [6], 19, 825; Thaller, *Sitzungsber. K. Akad. Wiss. Wien*, 1914, 123, 157; see Meyer, *Jahrb. Radioakt. Elektron.*, 1920, 17, 80. The International Committee on Chemical Elements give 16 5 years, see *J. Amer. Chem. Soc.*, 1923, 45, 867.

[9] Elster and Geitel, *Ann. Physik*, 1899, 69, 83; Giesel, *Ber.*, 1901, 34, 3772; 1902, 35, 102.

[10] Hofmann and Strauss, *Ber.*, 1901, 34, 8, 907, 3033; Hofmann and Wölfl, *ibid.*, 1902, 35, 692, 1453.

[11] Rutherford, *Phil. Trans.*, 1904, 204A, 169; *Phil. Mag.*, 1904, [6], 8, 636; 1905, [6], 10, 290; Hofmann, Gonder, and Wölfl, *Ber.*, 1903, 36, 1040; *Ann. Physik*, 1904, 15, 615; Meyer and von Schweidler, *Sitzungsber. K. Akad. Wiss. Wien*, 1905, 114, 1195; Elster and Geitel, *Physikal. Zeitsch.*, 1906, 7, 841; 1907, 8, 774; 1908, 9, 289; McLennan, *Phil. Mag.*, 1907, [6], 14, 760.

[12] Rossi, *Rend. Accad. Lincei*, 1907, 116, 701.

[13] Fajans, *Physikal. Zeitsch.*, 1911, 12, 369; Wertenstein, *Le Radium*, 1912, 9, 6; Makower, *Phil. Mag.*, 1916, [6], 32, 226.

[14] Wertenstein, *Compt. rend.*, 1915, 161, 696.

[15] Wood and Makower, *Phil. Mag.*, 1915, [6], 30, 811.

Whytlaw Gray observed in an old emanation tube a grey sub-metallic deposit consisting of about 0·001 mgm. of a mixture of radium D with 15 per cent. of the end-product of the series.[1]   On gently warming in an atmosphere of chlorine it changed to a pure white, crystalline, apparently homogeneous chloride, which, after solution in water, gave the triple crystalline nitrite with copper and potassium characteristic of lead.

Von Hevesy and Paneth obtained pure radium D in visible quantity, about 0·005 mgm., by allowing the emanation from 1 grm. of radium to decompose in a sealed quartz vessel, dissolving in nitric acid, and electrolysing.   Either radium D or radium D peroxide could be obtained, according to the conditions of the experiment, the peroxide forming a yellow deposit at the anode.[2]   By comparing the E.M.F. of the combination, radium D peroxide/radium D nitrate solution, with that of the combination, lead peroxide/radium D nitrate solution, and also the effect of the addition of lead ions to each, the electrochemical identity of radium D and lead was shown.

Radium D appears to be chemically inseparable from lead,[3] although Hofmann and Wölfl supposed that they had obtained a separation by the aid of Grignard's reaction.[4]   It can be precipitated by any reaction which precipitates lead provided a little lead is present.

The presence of lead in radium D may also be avoided by adding a solution of a few milligrams of aluminium chloride to a solution of an old preparation of radium which has had time to re-form radium D, and saturating with ammonia gas.   Radium D, E, F, B, C, and C″ are precipitated.   The last three quickly decay, and then radium E and F can be separated from the radium D by von Lerch's method on a nickel plate.[5]   From the purified solution radium D may be precipitated by ammonia along with aluminium hydroxide.[6]

In ammoniacal solution radium D is colloidal, but not in acid or neutral solution.[7]

Radium E.—Radium E is formed from radium D by a β-ray change, and should therefore have an atomic weight of 210.   Radium E also emits β-rays,[8, 9, 10] but of a much more penetrating type than radium D.   There is, in addition, a weak γ-radiation.[9, 11, 12]   The period is 5 days.[10, 13, 14]   Meyer and von Schweidler at first thought that

[1] Whytlaw Gray, *Nature*, 1913, **91**, 659
[2] von Hevesy and Paneth, *Ber.*, 1914, **47**, 2784 ; *Physikal. Zeitsch.*, 1914, **15**, 797.
[3] Szilard, *Compt. rend.*, 1908, **146**, 116 ; *Le Radium*, 1908, **5**, 1 ; Herszfinkel, *ibid.*, 1910, **7**, 198 ; Paneth and von Hevesy, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, 993 ; Staehling, *Compt. rend.*, 1913, **157**, 1430.
[4] Hofmann and Wolfl, *Ber.*, 1907, **40**, 2425 ; these experiments were repeated by Staehling, *loc. cit.*, with negative results.
[5] See Radium C.
[6] Russell, *An Introduction to the Chemistry of the Radioactive Substances* (John Murray), 1922, p. 156.
[7] Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, 1637.
[8] Danysz, *Le Radium*, 1913, **10**, 4 ; Mme. Curie, *ibid.*, 1911, **8**, 353.
[9] Schmidt, *Physikal. Zeitsch.*, 1907, **8**, 361.
[10] Rutherford, *Phil. Mag.*, 1905, [6], **10**, 290.
[11] Rutherford and Richardson, *ibid.*, 1913, [6], **26**, 324.
[12] Gray, *Proc. Roy. Soc.*, 1911, **85A**, 131.
[13] Meyer and von Schweidler, *Sitzungsber. K. Akad. Wiss. Wien*, 1905, **114**, 1195 ; 1906, **115**, 697.
[14] Antonoff, *Phil. Mag*, 1910, [6], **19**, 825.

radium E consisted of two products,[1] but this was shown to be wrong.[2, 3]

Radium E is one of the active constituents of radiolead, and can, of course, be obtained from radium D from any source, provided sufficient time has been allowed for its growth.[4] Polonium must first be separated from the solution by a bismuth plate, and the radium E then allowed to deposit on a nickel or silver plate, or the solution electrolysed, using a silver cathode.[5] In smaller quantity it may be deposited on tin, lead, or iron.[5]

Chemically it may be precipitated with hydrogen sulphide along with lead and radium D. Polonium is often brought down too, and radium E is probably the β-polonium of Giesel.[6]

Its decomposition voltage is the same as that of bismuth[7] from which it is, in fact, chemically inseparable.[2, 8] As is to be expected therefore, diffusion experiments show it to be tervalent.[9]

From a neutral solution of the nitrate a colloidal solution of the hydroxide may be obtained.[10]

Radium F, or Polonium.—The first new radioactive substance separated by Mme. Curie from pitchblende residues was polonium.[11] It was found to be precipitated along with bismuth by hydrogen sulphide, and could then be concentrated by three different methods :—

1. Sublimation of the sulphides *in vacuo*, the sublimate being more active than the residue.

2. Precipitation of the basic nitrate by water from solutions of the nitrate. The precipitate is more active than the dissolved salt.

3. Precipitation by hydrogen sulphide of a very strongly acid chloride solution. Again, the precipitate is more active than the solution.

The second method was apparently the most satisfactory.[12]

Marckwald obtained a very active substance, closely related to tellurium, by dipping a plate of copper, silver, or bismuth in the hydrochloric acid solution of active bismuth prepared from pitchblende. He called it radiotellurium.[13] Another method employed by him was the precipitation of active tellurium by stannous chloride. This was dissolved in a slightly acid solution and hydrazine chlorhydrate added. Inactive tellurium was thus precipitated, and the radiotellurium in the solution could then be reprecipitated by stannous chloride. Four mgm. of an intensely radioactive product were obtained by this method from two tons of pitchblende.[14]

[1] Meyer and von Schweidler, *Sitzungsber. K. Akad. Wiss. Wien*, 1906, 115, 697 ; *Physikal. Zeitsch.*, 1907, 8, 457.
[2] Antonoff, *Phil. Mag.*, 1910, [6], 19, 825.
[3] Fleck, *Trans. Chem. Soc.*, 1913, 103, 381.
[4] Rutherford and Richardson, *Phil. Mag.*, 1913, [6], 26, 324.
[5] Meitner, *Physikal. Zeitsch.*, 1911, 12, 1094.
[6] Giesel, *Ber.*, 1903, 36, 728 ; 1906, 39, 780.
[7] Paneth and von Hevesy, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, 122, 1037 ; von Hevesy, *Physikal. Zeitsch.*, 1914, 15, 797.
[8] Beer, *Le Radium*, 1914–1919, 11, 124.
[9] von Hevesy, *Physikal. Zeitsch.*, 1913, 14, 1202.
[10] Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, 122, 1637.
[11] M. and Mme. Curie, *Compt. rend.*, 1898, 127, 175.
[12] See Mme. Curie, *Traité de Radioactivité* (Gauthier-Villars), 1910, vol. i, pp. 149, 179.
[13] Marckwald, *Ber.*, 1902, 35, 2285, 4239 ; 1903, 36, 2662 ; *Physikal. Zeitsch.*, 1903, 4, 51 ; *Zeitsch. Elektrochem.*, 1903, 9, 698.
[14] Marckwald, *Ber.*, 1905, 38, 591.

It was ultimately shown that polonium and radiotellurium are identical, and the former name has been adopted for the substance.[1]

A study of the radium active deposit of slow rate of change showed that the product of the β-ray change of radium E, to which the name radium F was given, is in fact polonium.[2] Radium D, either from radio-lead or from old emanation tubes, is a convenient source of polonium. It may be separated by any of the methods already mentioned, or by electrolysing the nitrate of radiolead with a cathode potential of 0·08 volt referred to mercury. When it is not required to remove radium E higher current densities may be employed and potentials up to 0·5 volt. A further purification may be effected by distilling at about 1000° C. in a very slow current of hydrogen and carbon dioxide in a quartz tube. The polonium may be collected on a platinum or palladium plate placed where the temperature is 700°–900° C.[3, 4] The best yield, however, 80 per cent., is said to be obtained by rotating a copper plate in the solution.[3]

The atomic weight of polonium should be 210. It emits α-rays of range 3·58 cm. in air at normal temperature and pressure,[5] and 3·83 cm. at 15° C.[6] The initial velocity of the α-rays is $1·593 \times 10^9$ cm. per sec.[7] Debierne measured the rate of production of helium by polonium and obtained 0·589 cubic mm. in 587 days from a preparation initially emitting $5·99 \times 10^{10}$ α-particles per minute.[8]

Polonium in equilibrium with 1 grm. of radium, that is $2·19 \times 10^{-4}$ grm., generates 25·86 cal. per hour.[9]

Two mgm. of a very concentrated polonium preparation, probably containing 0·1 mgm. of polonium, when examined spectroscopically gave several new lines which may belong to polonium. Three were weak lines, 4642·0, 3913·6, and 3652·1 Å., and one strong, 4170·5 Å.[10]

The period of half-change of polonium is 136·5 days.[11]

[1] Debierne, *Jahrb. Radioakt. Elektron.*, 1904, **1**, 220 ; *Compt. rend.*, 1904, **139**, 281 ; Marckwald, *Jahrb. Radioakt. Elektron.*, 1905, **2**, 133 ; *Physikal. Zeitsch.*, 1906, **7**, 369 ; Curie, *ibid.*, 1906, **7**, 146 ; *Compt rend*, 1906, **142**, 273 ; Ewers, *Physikal. Zeitsch.*, 1906, **7**, 148.

[2] Giesel observed a small residual α-ray activity, *Ber.*, 1903, **36**, 2368 ; Rutherford at first called it radium E, *Phil. Mag.*, 1904, [6], **8**, 636 ; 1905, [6], **10**, 290 ; *Phil. Trans.*, 1905, **204A**, 169 ; see also Meyer and von Schweidler, *Sitzungsber. K. Akad. Wiss. Wien*, 1905, **114**, 1195 ; 1906, **115**, 63, 697 , Mme. Curie, *Physikal. Zeitsch.*, 1906, **7**, 180 ; Elster and Geitel, *ibid.*, 1907, **8**, 273, 776.

[3] Paneth and von Hevesy, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, 1049.

[4] Meitner, *Physikal. Zeitsch.*, 1911, **12**, 1094.

[5] van der Merwe, *Phil. Mag.*, 1923, [6], **45**, 379.

[6] Levin, *Amer. J. Sci.*, 1906, **22**, 8 ; Ewers, *Physikal. Zeitsch.*, 1906, **7**, 148 ; Kučera and Mašek, *ibid.*, 630 ; Geiger and Nuttall, *Phil. Mag.*, 1911, [6], **22**, 613 ; Meyer, *Jahrb. Radioakt. Elektron.*, 1920, **17**, 80.

[7] Irène Curie, *Compt. rend.*, 1922, **175**, 220.

[8] Debierne, *Ann. Physique*, 1914, [9], **2**, 428 ; see also Curie and Debierne, *Compt. rend.*, 1910, **150**, 386 ; *Le Radium*, 1910, **7**, 38 ; Rutherford and Boltwood, *ibid.*, 1911, **8**, 387.

[9] Soddy, *Ann. Rep. Chem. Soc.*, 1912, **9**, 311 ; see also Duane, *Compt. rend.*, 1909, **148**, 1665.

[10] Curie and Debierne, *Compt. rend.*, 1910, **150**, 386 ; *Le Radium*, 1910, **7**, 38.

[11] Giesel, *Ann. Physik*, 1899, **69**, 91 ; Meyer and von Schweidler, *Sitzungsber. K. Akad. Wiss. Wien*, 1905, **114**, 1195 ; 1906, **115**, 63 ; Rutherford, *Phil. Mag.*, 1905, [6], **10**, 290 ; Marckwald, Greinacher, and Herrmann, *Jahrb. Radioakt. Elektron.*, 1905, **2**, 136 ; Greinacher, *ibid.*, 139 ; Marckwald, *Ber.*, 1905, **38**, 591 ; Curie, *Compt. rend.*, 1906, **142**, 273 ; *Physikal. Zeitsch.*, 1906, **7**, 146, 180 ; Elster and Geitel, *ibid.*, 1908, **9**, 289 ; Regener, *Le Radium*, 1911, **8**, 458 ; *Ber. Deut. physikal. Ges.*, 1911, **13**, 1027 ; Waters, *Phil. Mag.*, 1910, [6], **19**, 905 ; von Schweidler, *Ber. Deut. physikal. Ges.*, 1912, **14**, 536. Recently the value 139·5 days has been given, Maracineanu, *Compt. rend.*, 1923, **176**, 1879, and the International Committee on Chemical Elements has adopted the value 136 days, see *J. Amer. Chem. Soc.*, 1923, **45**, 867.

Polonium tends to dissolve in platinum and palladium and, presumably, to form an alloy, since polonium vapour deposits preferentially on these two metals and cannot readily be removed by nitric acid.[1]

Polonium belongs to the sixth group of the Periodic Table, the sulphur group, and is probably identical in properties with radium A.[2] A careful study of the electrochemistry of polonium has been made, using gold electrodes in a 10^{-8} N solution, decinormal with respect to nitric acid.[3] It may be deposited on the cathode in the metallic state, or on the anode, probably as peroxide, according to conditions. The decomposition potential at the concentration studied is, for cathode deposition, 0·35 volt against mercury, and for anode deposition 1·05 volt. The normal cathode potential is calculated to be 0·57 volt. The calculated normal potential of polonium peroxide in 10^{-3} N nitric acid is 0·89 volt, whilst that of lead peroxide is 0·82.

Diffusion experiments in solution show that polonium is bivalent.[1]

Polonium has a tendency to form colloidal solutions when alkaline, neutral, or only faintly acid.[5]

Polonium Hydride has been prepared by generating hydrogen from magnesium in the presence of polonium. The polonium-magnesium mixture is formed by volatilising polonium and condensing on magnesium powder, which is then mixed to give a product of uniform activity. It can also be obtained by adding magnesium powder to a solution containing polonium, or by the electrolysis of a feebly acid solution with magnesium foil as cathode.

Polonium hydride decomposes spontaneously even more readily than bismuth hydride. It is decomposed by passing through unboiled distilled water, but not through air-free water. It is also decomposed by passing through decinormal sodium hydroxide or silver nitrate solutions, by drying, especially by phosphorus pentoxide, or by condensing in liquid air and re-evaporating.[6]

Radium G, or Uranium-Lead.—Since radium F emits an α-particle it must give rise to a product of atomic weight approximately 206, and, indeed, ionisation by recoil atoms from polonium has been observed. The range is 6 cm. in air at 1 mm. pressure, or less than 0·1 mm. at ordinary atmospheric pressure.[7] This is the only direct evidence hitherto obtained of the existence of radium G, the disintegration product of polonium, because, whatever its nature, it is not radioactive, and therefore cannot be detected by that means.

Theoretical considerations, which will be dealt with later,[8] indicate that an element which is formed from radium F by the emission of an α-particle may be supposed to occupy the same position as lead in the Periodic Table. Boltwood first made the suggestion that lead is the

[1] von Hevesy and Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, 1049; *Monatsh.*, 1915, **36**, 45.

[2] Muszkat and Herszfinkel, *J. Physique et Le Radium*, 1921, **2**, 15. For properties of polonium, see also Rutherford, *Nature*, 1910, **82**, 491.

[3] von Hevesy and Paneth, *Monatsh.*, 1915, **36**, 45.

[4] von Hovesy, *Physikal. Zeitsch.*, 1913, **14**, 49, 1202; *Phil. Mag.*, 1913, **25**, 390.

[5] Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, 2193; 1913, **122**, 1637; *Kolloid. Zeitsch.*, 1913, **13**, 1, 297; von Hevesy, *Physikal. Zeitsch.*, 1913, **14**, 1202.

[6] Paneth, *Ber.*, 1918, **51**, 1704; Paneth and Johannsen, *ibid.*, 1922, **55B**, 2622; see also Lawson, *Monatsh.*, 1915, **36**, 845.

[7] Bianu and Wertenstein, *Compt. rend.*, 1912, **155**, 475.

[8] See section on Isotopes.

end-product of the series,[1] lead being always found in the minerals containing radium.[2] Debierne observed that in a specimen of polonium the line in the spectrum, 4170·5 Å., disappeared completely after two years, whilst the strength of the lead lines increased.[3]

The fact that radium G, being formed from radium by five successive α-ray changes, should have an atomic weight of $226-5 \times 4 = 206$, might be expected to prove a difficulty in the way of accepting Boltwood's theory. Samples of lead from uranium-radium minerals have been found, however, to give an atomic weight of very little more than 206.[4,5]

Isotopes.—Until about 1912 or 1913 no systematic study was made of the chemical properties of the radio-elements, especially of the more transitory ones. It was natural, however, that some speculation should have arisen as to the effect of these successive radioactive changes on the residual atom. In 1906 Lucas,[6] from a study of von Lerch's experiments,[7] concluded that each radioactive element is more electronegative than its predecessor. This was subsequently shown to be incorrect,[8] and it was recognised that an α-ray transformation has a different effect from a β-ray change.[9] Ultimately Fajans formulated the following displacement rule : [10]

The product of an α-ray change has a position in the Periodic Table two places to the left of its predecessor, and the product of a β-ray change one place to the right.

It might, perhaps, be better expressed by saying that an α-ray change reduces the atomic number by two, whereas a β-ray change increases it by one. Whether the resulting element is more electropositive or more electronegative depends upon the position of the parent substance.

In the radium disintegration series there only appears to be one exception to this rule. Radium gives out both α- and β-rays. Application of the displacement rule would lead to the expectation of branching, 90–92 per cent. of the radium forming emanation by an α-ray change, and 8–10 per cent. forming a tervalent element by a β-ray change. Branching does not appear to take place, and no satisfactory explanation has been given, but it has been suggested that the β-radiation does not come from the nucleus but is a secondary radiation caused by a transference of energy from α-rays to electrons in the outer shells.[11]

[1] Boltwood, *Le Radium*, 1905, **2**, 400 ; *Amer. J. Sci*, 1907, **23**, 77.

[2] See also Holmes, *Proc. Roy. Soc.*, 1911, 85A, 248.

[3] Debierne, *Ann. Physique*, 1914, [9], **2**, 428.

[4] See section on Isotopes.

[5] Richards and Lembert, *Zeitsch. anorg. Chem.*, 1914, 88, 429 ; *J. Amer. Chem. Soc.*, 1914, 36, 1329 ; Richards and Wadsworth, *ibid.*, 1916, 38, 221, 1658, 2613 ; *Proc. Nat. Acad. Sci. U.S.A.*, 1916, **2**, 694 ; Richards, *Nature*, 1919, 103, 74, 93 ; Fajans, *Zeitsch. Elektrochem.*, 1914, 20, 449 ; Maurice Curie, *Compt. rend.*, 1914, 158, 1676 ; Hönigschmid and Horovitz, *ibid.*, 1914, 158, 1796 ; *Monatsh.*, 1915, 36, 355 ; Davis, *J. Physical Chem.*, 1918, **22**, 631, see *J. Chem. Soc.*, 1919, 116, Abs. ii, 107 ; Soddy, *Trans. Chem. Soc.*, 1919, 115, 1.

[6] Lucas, *Physikal. Zeitsch.*, 1906, **7**, 340.

[7] von Lerch, *Ann. Physik*, 1906, 20, 345.

[8] Fajans, *Le Radium*, 1912, **9**, 239 ; von Hevesy, *Physikal. Zeitsch.*, 1912, 13, 672.

[9] Fleck, *Chem. News*, 1913, 107, 95 ; von Hevesy, *Physikal. Zeitsch.*, 1912, 13, 672 ; 1913, 14, 49 ; *Le Radium*, 1913, 10, 65 ; Russell, *Chem. News*, 1913, 107, 49 ; Metzener, *Ber.*, 1913, 46, 979 ; Soddy, *The Chemistry of the Radio-Elements* (Longmans, Green & Co.), Part II, 1914.

[10] Fajans, *Ber. Deut. physikal. Ges.*, 1913, 15, 240 ; *Le Radium*, 1913, 10, 57, 61, 171 ; *Ber.*, 1913, 46, 422 ; *Physikal. Zeitsch.*, 1913, 14, 131, 136 ; Soddy, *Chem. News*, 1913, 107, 97 ; *Jahrb. Radioakt. Elektron.*, 1913, 10, 188 ; *Nature*, 1913, 91, 57.

[11] Hahn and Meitner, *Zeitsch. Physik*, 1920, **2**, 60.

Beginning with radium, the position of which can be fixed in the Periodic Table from a knowledge of its properties and atomic weight, the positions of all the succeeding products may be determined.

The atomic numbers are in brackets.

It will be noticed that the following groups are each composed of elements which occupy the same place in the Periodic Table—that is, which have the same atomic number [1] :—

In Group III, thallium and radium C''.

    ,,   ,,   IV, ordinary-lead, radium B, radium D, radium G, and the product of radium C''.

    ,,   ,,   V, bismuth, radium C, and radium E.

    ,,   ,,   VI, radium C', radium A, and radium F, or polonium.

It is an interesting fact that, as was seen in discussing the chemical properties of the radium disintegration series, in just these groups, wherever they have been amenable to chemical examination, the elements are shown to be chemically inseparable. That is, no matter what chemical or electrochemical treatment a mixture of such substances undergoes, their ratio remains the same at the end as at the beginning. If they are not radioactive, they are also, from most points of view, practically physically indistinguishable and inseparable. For

[1] Fajans, *Chem. Zeit.*, 1913, **37**, 242; *Ber. Deut. physikal. Ges.*, 1913, **15**, 240; Fleck, *Trans. Chem. Soc.*, 1913, **103**, 381, 1052.

example, melting-points,[1] molecular solubilities,[2, 3] decomposition potentials,[3] and atomic volumes,[4] appear to be the same. X-ray spectra appear to be identical,[5] and light spectra only display very minute differences when submitted to the most rigorous and careful measurement.[6] Owing to differences of atomic weight, however, it is possible that such methods as diffusion,[7] or distillation,[8] may prove effective in bringing about a separation. Such elements are said to be isotopic with one another.[9] The possibility of isotopes appears to be accounted for by the identity of the nuclear charge, and hence of atomic number. Instability of the atom or difference of atomic weight does not matter.[10]

Fajans prefers to describe the properties of isotopes, not as identical, but as equal, and considers it necessary to establish the limits within which the equality holds.[11]

Isotopism is not peculiar to radioactive substances. Many of the ordinary elements have been shown to consist of mixtures of inseparable isotopes, which thus behave as one element of a fixed mean atomic weight.[12]

Interesting consequences result from the phenomenon of isotopy. The existence of isotopes simplifies the study of the chemistry of what appears at first sight to be a large number of new elements brought to light by the study of radioactivity, because it reduces considerably the number of really new types.

Radium is isotopic with mesothorium, so that radium separated from minerals containing thorium will be contaminated for many years with mesothorium.[13]

The significance of the value for the atomic weight of lead from radium-containing minerals is at once evident. Moreover, the atomic weight of the end-product of thorium, thorium D, should be about 208, and be isotopic with lead. Samples of lead from thorium minerals

[1] Lembert, *Zeitsch. Elektrochem.*, 1920, 26, 59; Richards and Hall, *J. Amer. Chem. Soc.*, 1920, 42, 1550.

[2] Fajans and Fischler, *Zeitsch. anorg. Chem.*, 1916, 95, 284; Fajans and Lembert, *ibid.*, 297; Richards and Hall, *J. Amer. Chem. Soc.*, 1917, 39, 531; Richards and Schumb, *ibid.*, 1918, 40, 1403.

[3] Fajans, *Physikal. Zeitsch.*, 1914, 15, 935; *Jahrb. Radioakt. Elektron.*, 1917, 14, 314; 1918, 15, 101.

[4] Richards and Wadsworth, *J. Amer. Chem. Soc.*, 1916, 38, 1658

[5] Siegbahn and Stenström, *Compt. rend.*, 1917, 165, 428.

[6] Soddy and Hyman, *Trans. Chem. Soc.*, 1914, 105, 1402; Hönigschmid and Horovitz, *Monatsh.*, 1915, 36, 355; Richards and Lembert, *J. Amer. Chem. Soc.*, 1916, 38, 1329; Harkins and Aronberg, *Proc. Nat. Acad. Sci. U.S.A.*, 1917, 3, 710; *J. Amer. Chem. Soc.*, 1920, 42, 1328; Merton, *Proc. Roy. Soc.*, 1915, 91A, 198; 1920, 96A, 388; 1921, 100A, 84.

[7] Harkins, *Nature*, 1920, 105, 230; *Science*, 1920, 51, 289; *J. Amer. Chem. Soc.*, 1921, 43, 1803; Brönsted and von Hevesy, *Nature*, 1921, 107, 619.

[8] Brönsted and von Hevesy, *Nature*, 1920, 106, 144; *Zeitsch. physikal. Chem.*, 1921, 99, 189; *Phil. Mag.*, 1922, [6], 43, 31; Egerton, *Nature*, 1922, 110, 773.

[9] Soddy, *Chemistry of the Radio-Elements*, Part II (Longmans, Green & Co.), 1914; *Ann. Rep. Chem. Soc.*, 1916, 13, 245; *Trans. Chem. Soc.*, 1919, 115, 1; Fleck, *ibid.*, 1913, 103, 381; Paneth, *Jahrb. Radioakt. Elektron.*, 1914, 11, 451; the last paper gives a bibliography of the subject; see also Fajans, *Radioactivity*, translated by Wheeler and King (Methuen & Co., Ltd.), 1923, pp. 54, 94.

[10] Rutherford and Andrade, *Phil. Mag.*, 1914, 27, 854; see also van den Broek, *Physikal. Zeitsch.*, 1913, 14, 32.

[11] Fajans, *Physikal. Zeitsch.*, 1916, 17, 1; but see von Hevesy and Paneth, *ibid.*, 1916, 17, 4.

[12] Aston, *Isotopes* (Arnold), 1922.

[13] Strong, *J. Amer. Chem. Soc.*, 1921, 43, 440.

have given values approaching 208.[1] Ordinary lead, in view of the fractional value of its atomic weight, is probably a mixture of these.[2]

Von Hevesy and Paneth have studied the E.M.F.'s of the following galvanic cells [3]:—

i. $Pt,PbO_2/RaG(NO_3)_2$, HNO_3, $RaGO_2$ /Comparison electrode;

ii. $Pt,RaGO_2/Pb(NO_3)_2$, $10^{-3}N$ HNO_3. $10^{-3}N$ PbO_2 (saturated) /Comparison electrode;

iii. $Pt,RaGO_2/RaG(NO_3)_2$, $10^{-3}N$ HNO_3, $10^{-3}N$ $RaGO_2$ (saturated) /Comparison electrode;

and also a cell with radium G peroxide and lead peroxide at different electrodes. All showed that, within the limits of experimental error, there was, electrochemically, no difference between radium G and lead.

It is necessary to distinguish between the association of isotopic bodies and occlusion—for example, in cases of precipitation. In the case of an isotopic mixture the same proportions are maintained in the precipitated or crystallised solid as in the solution from which it is derived,[4] or in fact in any two phases in equilibrium with each other [5]— for instance, active lead nitrate solution in contact with lead amalgam.[6]

As regards occlusion or adsorption, it has been shown that a radio-element is carried down from an extremely dilute solution with a precipitate of an ordinary element when, under the existing conditions, the radio-element itself would be precipitated if present in sufficient concentration. The precipitation of a radio-element is governed not so much by the nature of the ions in solution as by the negative part of the precipitate.[7]

Radioactive isotopes appear to have a sphere of future usefulness as both qualitative and quantitative indicators of the presence of inactive substances. Their employment in this way has already been developed to some extent in several directions.[8] They may be applied, for example, to the determination of the solubility of very insoluble substances. The solubility of lead chromate or sulphide can be found by mixing a known quantity of a soluble lead salt with a radioactive isotope in solution, determining the activity of a known amount of the product resulting on evaporation, precipitating the chromate or sulphide, washing, and shaking up with water. The amount of indicator in a certain fraction of solution is then determined by evaporating to dryness and measuring the activity, and as this will bear the same

[1] Soddy and Hyman, *Trans. Chem. Soc.*, 1914, **105**, 1402; Soddy, *Ann. Rep. Chem. Soc.*, 1916, **13**, 247; Hönigschmid, *Zeitsch. Elektrochem.*, 1917, **23**, 161; 1919, **25**, 91; Fajans, *ibid.*, 1918, **24**, 163.

[2] See Soddy, *Ann. Rep. Chem. Soc.*, 1918, **15**, 201.

[3] von Hevesy and Paneth, *Monatsh.*, 1915, **36**, 795.

[4] von Hevesy and Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, 993; *Monatsh.*, 1913, **34**, 1393; Staehling, *Compt. rend.*, 1913, **157**, 1430; Richards and Hall, *Proc. Nat. Acad. Sci. U.S.A.*, 1917, **3**, 339.

[5] Stromholm and Svedberg, *Zeitsch. anorg. Chem.*, 1909, **63**, 200.

[6] Klemensiewicz, *Compt. rend.*, 1914, **158**, 1889.

[7] Fajans and Beer, *Ber.*, 1913, **46**, 3486; Paneth, *Physikal. Zeitsch.*, 1914, **15**, 924; *Jahrb. Radioakt. Elektron.*, 1914, **11**, 451; Fajans and Richter, *Ber.*, 1915, **48**, 700; Horovitz and Paneth, *Zeitsch. physikal. Chem.*, 1915, **89**, 513.

[8] See Paneth, *Zeitsch. angew. Chem.*, 1922, **35**, 549, who has given a comprehensive account of the uses to which they may be put; Fajans, *Radioactivity*, translated by Wheeler and King (Methuen & Co., Ltd.), 1923, p. 105.

ratio to the lead as initially, the solubility of the sparingly soluble lead salt can thus be calculated.[1] In a similar manner rates of solution can be determined.[2]

The amount of adsorption of certain substances by precipitates, or colloids, or filter-paper, may be measured by the activity of the radio-active isotope mixed with it.[3] It is also possible to measure the surface of powders,[4] to study the conditions of formation of unstable compounds, such as bismuth hydride, and the extent to which they are formed,[5] to study the behaviour of ions in solution [6] and of substances at higher dilution than can be recognised by any other method,[7] to determine the extent of the self-diffusion of metals such as lead and of salts near the point of fusion,[8] and so on.

The Origin of Radium.—Compared with the length of geological periods the life of radium is very short. It seems unlikely, therefore, that radium is a primary element. Rather is it to be expected that it derives from some other radioactive element of very much longer life. It has been indicated already that radium is always found associated with uranium except where obviously subjected to alteration, and it was early suggested that uranium, which was shown by Becquerel to be radioactive, is the original parent of radium. This conclusion is borne out by the fact that in old unaltered minerals, in which it may be supposed that radioactive equilibrium has been reached, the ratio of radium to uranium is practically constant, being $3 \cdot 40 \pm 0 \cdot 03 \times 10^{-7}$ on the International Radium Standard.[9]

The constancy of this ratio was first observed by several independent workers in 1904. McCoy [10] compared the activity of thin films of mineral with that of the uranium contained in it. Boltwood [11] and Strutt [12] determined directly the quantity of radium by estimating the emanation released on dissolving in acid.

The measurements of later investigators substantially confirmed the

[1] von Hevesy and Paneth, *Zeitsch. anorg. Chem.*, 1913, 82, 323.

[2] von Hevesy and Róna, *Zeitsch. physikal. Chem.*, 1915, 89, 294.

[3] Horovitz and Paneth, *ibid.*, 1915, 89, 513 ; Paneth, *Physikal. Zeitsch.*, 1914, 15, 924 ; *Jahrb. Radioakt. Elektron.*, 1914, 11, 451.

[4] Paneth, *Zeitsch. Elektrochem.*, 1922, 28, 113 ; Paneth and Vorwerk, *Zeitsch. physikal. Chem.*, 1922, 101, 445.

[5] Paneth, *Zeitsch. Elektrochem.*, 1918, 24, 298 ; *Ber.*, 1918, 51, 1704, 1728 ; Paneth and Winternitz, *ibid.*, 1728 ; Paneth and Fürth, *ibid.*, 1919, 52B, 2020 ; Paneth and Nörring, *ibid.*, 1920, 53B, 1693.

[6] von Hevesy, *Physikal. Zeitsch.*, 1915, 16, 52 ; von Hevesy and Zechmeister, *Ber.*, 1920, 53B, 410 ; *Zeitsch. Elektrochem.*, 1920, 26, 151.

[7] von Hevesy, *Zeitsch. Elektrochem.*, 1912, 18, 546 ; 1913, 19, 291 ; *Physikal. Zeitsch.*, 1913, 14, 49, 1202 ; 1914, 15, 797 ; *Sitzungsber. K. Akad. Wiss. Wien*, 1918, 127, 1787 ; Paneth, *Kolloid. Zeitsch.*, 1913, 13, 1, 297 ; *Jahrb. Radioakt. Elektron.*, 1914, 11, 451 ; von Hevesy and Paneth, *Physikal. Zeitsch.*, 1915, 16, 45 ; *Monatsh.*, 1915, 36, 45 ; Herzfeld, *Physikal. Zeitsch.*, 1913, 14, 29 ; Godlewski, *Kolloid. Zeitsch.*, 1914, 14, 229 ; Lachs, *ibid.*, 1917, 21, 165 ; Lachs and Herszfinkel, *J. Physique et Le Radium*, 1921, [6], 2, 319.

[8] von Hevesy, *Zeitsch. Elektrochem.*, 1920, 26, 363 ; *Zeitsch. Physik*, 1920, 2, 148 ; Gróh and von Hevesy, *Ann. Physik*, 1920, [4], 63, 85.

[9] Lind and Roberts, *J. Amer. Chem. Soc.*, 1920, 42, 1170 ; see also Rutherford, *Phil. Mag.*, 1914, [6], 28, 320.

[10] McCoy, *Ber.*, 1904, 37, 2641 ; see also McCoy and Ross, *J. Amer. Chem. Soc.* ,1907, 29, 1698.

[11] Boltwood, *Amer. J. Sci.*, 1904, 18, 97 ; *Nature*, 1904, 70, 80 ; *Le Radium*, 1904, 1, 45 ; *Phil. Mag.*, 1905, [6], 9, 599 ; see also Rutherford and Boltwood, *Amer. J. Sci.*, 1905, 20, 55 ; 1906, 22, 1 ; *Le Radium*, 1906, 3, 197.

[12] Strutt, *Nature*, 1904, 70, 222 ; *Proc. Roy. Soc.*, 1905, 76A, 88.

earlier results but revealed certain exceptions.[1] Secondary minerals, such as autunites and chalcolites of comparatively recent formation, give a low value for the ratio. This may be due to either or both of the following causes : (1) to the recent formation of the mineral, so that it has not yet reached radioactive equilibrium, or (2) to the loss of radium by percolating water or some other chemical agency. Certain pitch-blendes, and even a chalcolite, have, however, been found to give a higher value than normal, but it has been suggested that here also alteration may have taken place, radium being transferred by water from one part of the mineral to another.

Experiments were made to determine whether radium is directly produced from uranium. Soddy used a uranium nitrate solution freed from radium by precipitating barium as sulphate in the solution. A steady growth of radium was observed, but much slower than was expected.[2] Boltwood, on the other hand, by using uranium nitrate purified by a large number of recrystallisations, obtained no evidence of the production of radium from 100 grm. of uranium nitrate over 390 days.[3]

It was evident from these experiments that at least one radio-active substance of very slow rate of transformation must come between uranium and radium. This conclusion was verified by the discovery of ionium.[4] All uranium minerals are found to contain ionium, and ionium freed from radium grows radium at a rapid rate. Ordinary commercial preparations of uranium nitrate slowly grow radium owing to the ionium initially present in them, but no growth is observed when the latter is completely removed, thus indicating a much longer life for ionium than for radium.[5]

Ionium, however, is not the only substance between uranium and radium. So far as is known, the following suggested scheme represents the line of direct descent from uranium to radium [6] :—

$$\alpha \qquad \beta \qquad \beta \qquad \alpha \qquad \alpha$$
Uranium I→Uranium X$_1$→Uranium X$_2$→Uranium II→Ionium→Radium.
$$\text{VI.} \qquad \text{IV.} \qquad \text{V.} \qquad \text{VI.} \qquad \text{IV.} \qquad \text{II.}$$
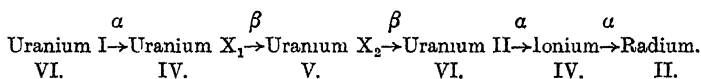
The Roman numerals below the names of the elements indicate the group in the Periodic Table to which these belong.

[1] Gleditsch, *Compt. rend.*, 1909, 148, 1451 ; 149, 267 ; *Le Radium*, 1909, 6, 165 ; 1911, 8, 256 ; *Archiv Math. Naturvid. Christiania*, 1919, 36, No. 1 ; Soddy, *Nature*, 1910, 84, 296 ; Soddy and Pirret, *Phil. Mag.*, 1910, [6], 20, 345 ; 1911, [6], 21, 652 ; Soddy, *ibid.*, 1919, [6], 38, 483 ; Soddy and Hitchins, *ibid.*, 1915, [6], 30, 209 ; Russell, *Nature*, 1910, 84, 238 ; Marckwald and Russell, *Jahrb. Radioakt. Elektron.*, 1911, 8, 457 ; *Chem. News*, 1911, 103, 277 ; *Ber.*, 1911, 44, 771 ; Heimann and Marckwald, *Jahrb. Radioakt. Elektron.*, 1913, 10, 299 ; Rutherford, *Phil. Mag.*, 1914, [6], 28, 320 ; Lind and Whittemore, *J. Amer. Chem. Soc.*, 1914, 36, 2066 ; Becker and Jannasch, *Jahrb. Radioakt. Elektron.*, 1915, 12, 1 ; Johnstone and Boltwood, *Phil. Mag.*, 1920, [6], 40, 50 ; *Amer. J. Sci.*, 1920, 50, 1 ; Lind and Roberts, *J. Amer. Chem. Soc*, 1920, 42, 1170.

[2] Soddy, *Nature*, 1904, 70, 30 ; 1905, 71, 294 ; *Phil. Mag.*, 1905, [6], 9, 768 ; Soddy and Mackenzie, *ibid.*, 1907, [6], 14, 272.

[3] Boltwood, *Amer. J. Sci.*, 1905, 20, 239.

[4] Boltwood, *ibid.*, 1907, 24, 370 ; 1908, 25, 365, 493 ; *Physikal. Zeitsch.*, 1907, 8, 884.

[5] Soddy and Mackenzie, *Phil. Mag.*, 1907, [6], 14, 272 ; Soddy, *ibid.*, 1908, [6], 16, 632 ; 1909, [6], 18, 846 ; *Proc. Physical Soc.*, 1909–1910, 22, 42 ; Soddy and Hitchins, *Phil. Mag.*, 1915, [6], 30, 209.

[6] Soddy, *Ann. Rep. Chem. Soc.*, 1912, 9, 321 ; 1913, 10, 268.

THE PREDECESSORS OF RADIUM.

Uranium I.—It was in uranium that the phenomenon of radioactivity was first recognised.[1] This element gives out α-rays. From a comparison of the ionising power of uranium deprived as far as possible of all its products, with the ionising power of the other α-radiating members of the series, it was seen that uranium must be emitting twice the number of α-rays given out by any one of the substances in equilibrium with it.[2] This was confirmed by the direct enumeration by the scintillation method of the α-particles from thin films of uranium and from mineral films containing a known quantity of uranium.[3, 4] Determinations of the range also seemed to indicate that α-particles of two slightly differing ranges are emitted,[5] one of range 2·5 cm. at 15° C., and the other 2·9 cm. This indicates the presence in uranium of two separate elements, each emitting α-rays. No chemical means has been found to separate them, nor can they be separated by diffusion in solution, being of the same valency.[6] Therefore they are probably isotopic, and it is obvious, by the displacement rule, that one cannot be the immediate successor of the other. By counting the number of α-particles per gram of uranium, and assuming that half come from the primary element, a period of approximately 5×10^9 years for uranium I may be deduced.[3, 7] A similar value is obtained by comparing the weights of radium and uranium in equilibrium with one another.[8] The most recent value given is $4·67 \times 10^9$ years.[9]

Production of helium from uranium has been observed.[10]

The chemistry of uranium and its compounds is dealt with elsewhere.[11]

Uranium X_1.—Ordinary uranium preparations emit β- and γ-rays, as well as α-rays. Crookes showed, however, that uranium could be obtained photographically inactive, that is freed from β-rays, by precipitating with ammonium carbonate and dissolving in excess of the reagent. A small insoluble residue, consisting probably chiefly of traces of iron, contained the β- and γ-activity.[12] In fact, the separation is helped by the addition of a little iron. Becquerel precipitated the same substance along with barium sulphate.[13] It was at first known as uranium X,

[1] Becquerel, *Compt. rend.*, 1896, **122**, 420, 501, 559, 689, 762, 1086.

[2] Boltwood, *Amer. J. Sci.*, 1908, **25**, 269.

[3] Geiger and Rutherford, *Phil. Mag.*, 1910, [6], **20**, 691 ; *Le Radium*, 1910, **7**, 225.

[4] Brown, *Proc Roy. Soc.*, 1910, **84A**, 151.

[5] Geiger and Nüttall, *Phil. Mag.*, 1912, [6], **23**, 439 ; see also Foch, *Le Radium*, 1911, **8**, 101 ; Friedmann, *Sitzungsber. K. Akad. Wiss. Wien*, 1911, **120**, 1361 ; Meyer and Paneth, *ibid.*, 1912, **121**, [2a], 1403.

[6] von Hevesy and Putnoky, *Physikal. Zeitsch.*, 1913, **14**, 63 ; *Phil. Mag.*, 1913, [6], **25**, 415.

[7] See also Meyer, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, **122**, [2a], 1085.

[8] Geiger and Nuttall, *loc. cit.* ; see also McCoy, *Phys. Review*, 1913, **1**, 401.

[9] See International Committee on Chemical Elements, *J. Amer. Chem. Soc.*, 1923, **54**, 867.

[10] Soddy, *Nature*, 1908, **79**, 129 ; *Le Radium*, 1908, **5**, 361 ; *Physikal. Zeitsch.*, 1909, **10**, 41.

[11] See Vol. VII, Part III.

[12] Crookes, *Proc. Roy. Soc.*, 1900, **66**, 409 ; see also Soddy, *Phil. Mag.*, 1909, [6], **18**, 861.

[13] Becquerel, *Compt. rend.*, 1900, **131**, 137 ; 1901, **133**, 977 ; Soddy, *Trans. Chem. Soc.*, 1902, **81**, 860 ; Berry, *ibid.*, 1910, **97**, 196 ; Soddy and Russell, *Phil. Mag.*, 1909. [6], **18**, 620.

but, later, when it was found to be accompanied by another new radio-active substance, the two were distinguished as uranium X_1 and uranium X_2 respectively.

Uranium X_1 can also be obtained by extracting uranium salt solutions with ether or other organic solvents, uranium X_1 remaining in the aqueous layer.[1] On recrystallising uranyl nitrate most of the uranium X_1 remains in the mother liquor.[2] Keetman suggested for the separation the addition of a little cerium salt to the uranium solution, and its precipitation in acid solution with hydrofluoric acid.[3] It may also be absorbed by charcoal,[4] basic ferric acetate,[5] and by various oxides, sulphates, sulphides, and gelatinous silica.[6] The separation of uranium and uranium X_1 has been unsuccessfully attempted by cathodic pulverisation *in vacuo*.[7]

Hahn suggested the following method as the one most favourable for the separation of uranium X_1.[8] Uranium nitrate is first fractionally crystallised from water to remove the greater part of the uranium. Ferric chloride is then added to the mother liquor in the proportion of 50 mgm. to 100 grm. of uranium nitrate, and the iron is then separated from the diluted solution by adding ammonium hydroxide and ammonium carbonate with careful warming. Uranium X_1 is adsorbed by the iron if no weighable quantity of thorium be present. It may be freed from uranium by redissolving and reprecipitating with ammonia and ammonium carbonate.

The period of half-change of uranium X_1 is $23 \cdot 82 \pm 0 \cdot 075$ days.[9] It emits soft β-rays,[10] so soft that they were at first taken for α-rays.[11] A hard β-radiation ascribed to it was afterwards found to be due to uranium X_2.[12] It also gives very weak γ-rays.[13]

Diffusion experiments in solution show that uranium X_1 is tetravalent.[14] It is isotopic with thorium[15] and ionium,[16] and therefore has the same chemical properties.

[1] Lloyd, *J. Physical Chem.*, 1910, 14, 509 ; Moore and Schlundt, *Phil. Mag.*, 1906, [6], 12, 393.

[2] Soddy and Russell, *loc. cit.* : see also Godlewski, *Phil. Mag.*, 1905, [6], 10, 45.

[3] Keetman, *Jahrb. Radioakt. Elektron.*, 1909, 6, 268. Guy and Russell add thorium nitrate, since thorium is the isotope, *Trans. Chem. Soc.*, 1923, 123, 2618.

[4] Ritzel, *Zeitsch. physikal. Chem.*, 1909, 67, 724; Freundlich and Kaempfer, *ibid.*, 1915, 90, 681 ; Freundlich, Neumann, and Kaempfer, *Physikal. Zeitsch.*, 1914, 15, 537.

[5] Brown, *Trans. Chem. Soc.*, 1922, 121, 1736 ; Szilard, *Compt. rend.*, 1909, 149, 113.

[6] Wojtasrewski, *Le Radium*, 1913, 10, 363 (Abs.).

[7] von Sensel, *Zeitsch. physikal. Chem.*, 1910, 71, 563.

[8] Hahn, *Ber.*, 1921, 54B, 1134; Meyer and von Schweidler, *Jahrb. Radioakt. Elektron.*, 1909, 6, 390.

[9] Kirsch, *Sitzungsber. K. Akad. Wiss. Wien*, 1920, 129, 309 ; see also Rutherford and Soddy, *Phil. Mag.*, 1903, [6], 5, 441 ; Soddy and Russell, *ibid.*, 1910, [6], 19, 847.

[10] Soddy, *Trans. Chem. Soc.*, 1902, 81, 860 ; *Nature*, 1909, 80, 37 ; *Phil. Mag.*, 1909, [6], 18, 858 ; Rutherford and Grier, *ibid.*, 1902, [6], 4, 323 ; Levin, *Physikal. Zeitsch.*, 1907, 8, 585 ; 1908, 9, 655 ; Hahn and Rothenbach, *ibid.*, 1919, 20, 194.

[11] Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1907, 116, [2a], 109 ; Levin, *Physikal. Zeitsch.*, 1907, 8, 129.

[12] See Fajans and Göhring, *Physikal. Zeitsch.*, 1913, 14, 877.

[13] Soddy, *Trans. Chem. Soc.*, 1902, 81, 860 ; *Phil. Mag.*, 1910, [6], 20, 342 ; Soddy and Russell, *Nature*, 1909, 80, 7 ; *Physikal. Zeitsch.*, 1909, 10, 249 ; *Phil. Mag.*, 1909, [6], 18, 620 ; Eve, *Physikal. Zeitsch.*, 1907, 8, 185 ; Baeyer, Hahn, and Meitner, *ibid.*, 1914, 15, 649 ; Richardson, *Phil. Mag.*, 1914, [6], 27, 252.

[14] von Hevesy, *Physikal. Zeitsch.*, 1913, 14, 49, 1202.

[15] Fleck, *Trans. Chem. Soc.*, 1913, 102, 381.

[16] Soddy, *ibid.*, 1911, 99, 82.

Uranium X₂, or Brevium.—On shaking a feebly acid solution of iron containing uranium X_1 in a clean lead crucible, and then removing the liquid, the crucible shows a very penetrating β-activity which at first falls very rapidly in value. This is ascribed to uranium X_2, the product of uranium X_1.[1,2] Uranium X_2 has a period of 1·15 minutes,[1,3,4,5] and emits both β- and γ-rays,[6] the β-rays probably being more penetrating than those emitted by uranium X_1.

Fajans and Göhring[1] gave to it the name of brevium. It is chemically similar to both tantalum and bismuth, its position, according to the displacement rule, being in Group V. It may be separated from uranium X_1 by precipitating along with bismuth oxychloride,[3] or with tantalic acid.[1] The iodide is less volatile than bismuth iodide.

Uranium II.—The product of uranium X_2 ought to be an isotope of uranium I, with an atomic weight of about 234. This is considered to be the second α-ray-producing substance present in uranium, and inseparable from it, which has already been mentioned, and has been given the name uranium II.[1] The range of its α-particles is 2·9 cm., and by calculation from the Geiger-Nuttall relation between range and period,[7] the period of uranium II is probably in the neighbourhood of 2×10^6 years.[8] The quantity of uranium II in equilibrium with uranium I will be about $\frac{1}{1000}$ of the weight of the latter, and so will not materially influence its atomic weight.

There is no evidence of the growth of an α-radiation from uranium X_1.[9]

Unsuccessful attempts have been made to separate the two uraniums by diffusion in solution.[10]

Ionium.—The failure to grow radium from purified uranium led to a search for the immediate parent of radium, resulting in the discovery of ionium. Boltwood separated from carnotite a substance which grew radium at a rapid rate, and which he thought at first to be identical with actinium.[11] It was shown, however, that, although ordinary actinium preparations grow radium, it is not derived from actinium itself, but from a new substance separated with it and chemically different,[12] to which Boltwood gave the name of ionium.[13] It gives α-rays of range 3·07 cm. at 15° C., and of initial velocity $1·46 \times 10^9$ cm. per sec.,[8,14] and also γ-rays.[8]

Ionium can be obtained from pitchblende by any chemical process which will also give thorium, and it has not been found possible to separate ionium from the thorium always present to some extent in

[1] Fajans and Göhring, loc. cit.

[2] Hahn and Rothenbach, Physikal. Zeitsch., 1919, 20, 196.

[3] Fleck, Phil. Mag., 1913, [6], 26, 528.

[4] Hahn and Meitner, Physikal. Zeitsch., 1913, 14, 758.

[5] Guy and Russell found 1·175 min., Trans. Chem. Soc., 1923, 123, 2618.

[6] Richardson, Phil. Mag., 1914, [6], 27, 252.

[7] Geiger and Nuttall, Phil. Mag., 1912, [6], 23, 439.

[8] See Meyer, Jahrb. Radioakt. Elektron., 1920, 17, 80.

[9] Soddy, Phil. Mag., 1909, [6], 18, 858 ; Proc. Physical Soc., 1909–1910, 22, 57.

[10] Lachs, Nadratowska, and Wertenstein, Compt. rend. Soc. Sci. Warsaw, 1917, 9, 67, see J. Chem. Soc., 1918, 114, Abs. ii, 213.

[11] Boltwood, Amer. J. Sci., 1906, 22, 537.

[12] Rutherford, Nature, 1907, 75, 270 ; 76, 661 ; Phil. Mag., 1907. [6], 14, 733.

[13] Boltwood, Amer. J. Sci., 1907, 24, 370 ; 1908, 25, 365.

[14] Geiger and Nuttall, Phil. Mag., 1911, [6], 22, 613.

uranium minerals.[1]   This would suggest that ionium is isotopic with thorium, and, therefore, also with uranium X_1.   That it should be isotopic with uranium X_1 is in accordance with the displacement rule.[2] The isotopy with thorium is confirmed by the result of the spectroscopic examination of thorium preparations rich in ionium, which give only the spectrum of thorium.[3]   The chemical reactions of ionium, therefore, are exactly the same as those of thorium.[4]

Uranium X_1 may be used as an indicator for ionium when estimating the latter in terms of the equilibrium quantity contained in uranium minerals.[5]

The period of ionium is 9×10^4 years.[6]

From its connection with uranium and radium the atomic weight of ionium should be approximately 230.   Honigschmid found 231·5 for thorium-ionium mixtures obtained from minerals poor in thorium.[7]

The production of helium from ionium has been observed.[8]

Diffusion experiments in solution show that ionium is tetravalent, which is in accordance with its position in the Periodic Table.[9]

BRANCHING BETWEEN URANIUM AND RADIUM.

Uranium Y and Uranium Z.—A constant constituent of uranium minerals, in quantity proportional to the uranium present, is actinium.[10] This suggests that actinium is a product of uranium.[11]   It seems unlikely, however, that it can find a position in the direct line of descent through radium.   The only alternative conclusion is that the uranium series branches, one branch giving radium and its products, and the other actinium.[12]

In 1911 Antonoff found that uranium X_1 shows at first a rapidly falling soft β-ray activity, and attributed the effect to a new radioactive element which he called uranium Y.[12, 13]   Fleck doubted its existence,[14] but it now appears to be definitely established.[15]

It is isotopic with uranium X_1, and, according to Guy and Russell,

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[1] Boltwood, *loc. cit.*; Hahn, *Ber.*, 1907, **40**, 4415; Marckwald and Keetman, *ibid.*, 1908, **41**, 49; Keetman, *Jahrb. Radioakt. Elektron.*, 1909, **6**, 265; see also Szilard, *Le Radium*, 1909, **6**, 80; Meitner, *Physikal. Zeitsch.*, 1915, **16**, 4.

[2] See table showing connection between uranium and radium, p. 305.

[3] Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, [2a], 1075; Russell and Rossi, *Proc. Roy. Soc.*, 1912, **87A**, 478.

[4] See Caven, Vol. V. of this series.

[5] Rona, *Ber.*, 1922, **55B**, 294.

[6] Soddy, *Le Radium*, 1910, **7**, 295; *Nature*, 1912, **89**, 203; *Phil. Mag.*, 1919, [6], **38**, 483; Soddy and Hitchins, *ibid.*, 1915, [6], **30**, 209; Piutti, *Le Radium*, 1911, **8**, 204; Russell and Rossi, *loc. cit.*; Meyer, *Jahrb. Radioakt. Elektron.*, 1920, **17**, 80; *Monatsh.*, 1916, **37**, 347.   The International Committee on Chemical Elements, *J. Amer. Chem. Soc.*, 1923, **45**, 867, gives $6·9 \times 10^4$ years.

[7] Honigschmid, *Zeitsch. Elektrochem.*, 1916, **22**, 18; Honigschmid and Horovitz, *Monatsh.*, 1916, **37**, 335.

[8] Boltwood, *Le Radium*, 1911, **8**, 104; *Proc. Roy. Soc.*, 1911, **85A**, 77.

[9] von Hevesy, *Physikal. Zeitsch.*, 1913, **14**, 49.

[10] Meyer and Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1919, **128**, [2a], 909.

[11] McCoy and Ross, *J. Amer. Chem. Soc.*, 1907, **29**, 1698.

[12] Antonoff, *Phil. Mag.*, 1911, [6], **22**, 419; 1913, [6], **26**, 1058; see also Johnstone and Boltwood, *ibid.*, 1920, [6], **40**, 50; *Amer. J. Sci.*, 1920, **50**, 1.

[13] Antonoff, *Le Radium*, 1913, **10**, 406.

[14] Fleck, *Phil. Mag.*, 1913, [6], **25**, 710.

[15] Soddy, *ibid.*, 1914, [6], **27**, 215; Hahn and Meitner, *Physikal. Zeitsch.*, 1914, **15**, 236.

has a period of half-change of 27·5 hours,[1] but somewhat variable values have been given.[2, 3, 4]

In order to obtain it as free as possible from uranium X_1, a little iron should be precipitated with ammonia and ammonium carbonate in uranium nitrate solution. This frees the uranium from both uranium X_1 and uranium Y, but after a few days the amount of uranium Y has risen to its maximum value again, whilst very little uranium X_1 has been formed, and by repeating the precipitation, iron containing all the uranium Y and very little uranium X_1 is obtained.[3] Uranium X_1 and uranium Y may also be separated together by precipitation along with cerous fluoride. They can then be removed from the cerium by adding a little zirconium salt and precipitating with sodium hypo-phosphate, $NaHPO_3.3H_2O$.[5]

From the first it was thought probable that uranium Y formed a branch of the uranium-radium series,[6] and the proportion which it bears to uranium X_1 seemed to indicate that it is the first member of the actinium series. As it is isotopic with uranium X_1, it is probably formed by an α-ray change from uranium I or uranium II, the latter view being the one more generally accepted. The fraction of the uranium breaking up to form uranium Y is about 3 per cent.[1, 5, 7, 8]

Uranium Y, being isotopic with uranium X_1, is tetravalent, and since it gives β-rays it is unlikely, by the group displacement law, that it will be transformed directly into tervalent actinium. An α-ray product should lie between them, and this conclusion was confirmed by the discovery of ekatantalum or protoactinium, which is the parent of actinium.[9]

The following alternative schemes have been suggested [10, 11] :—

Uranium I→Uranium X_1→Uranium X_2→Uranium II→Ionium

$\downarrow$ $\downarrow$

Uranium Y →Protoactinium →Actinium.   Uranium Y→Protoactinium→Actinium
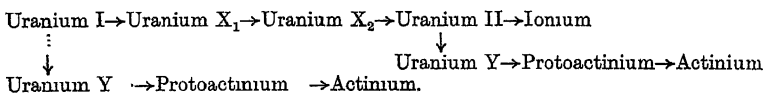
Still another element, to which the name uranium Z has been given, has been found in ordinary uranium salts.[12] It is precipitated

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[1] Guy and Russell, *Trans. Chem. Soc.*, 1923, **123**, 2618.

[2] Antonoff, *Phil. Mag.*, 1911, [6], **22**, 419; 1913, [6], **26**, 1058; see also Johnstone and Boltwood, *ibid.*, 1920, [6], **40**, 50; *Amer. J. Sci.*, 1920, **50**, 1.

[3] Antonoff, *Le Radium*, 1913, **10**, 406.

[4] Kirsch, *Sitzungsber. K. Akad. Wiss. Wien*, 1920, **129**, [2a], 309; see also Hahn and Meitner, *loc. cit.*; *Naturwiss.*, 1919, **7**, 611; *Ber.*, 1919, **52B**, 1812; *Zeitsch. Physik*, 1922, **8**, 202.

[5] Kirsch, *loc. cit.*

[6] Antonoff, *Phil. Mag.*, 1911, [6], **22**, 419; 1913, [6], **26**, 1058.

[7] See Hahn and Meitner, *Physikal. Zeitsch.*, 1919, **20**, 529.

[8] Widdowson and Russell, *Phil. Mag.*, 1923, [6], **46**, 915.

[9] Soddy, Cranston, and Hitchins, *Proc. Roy. Soc.*, 1918, **94A**, 384; *Nature*, 1918, **100**, 498; Hahn and Meitner, *Physikal. Zeitsch.*, 1918, **19**, 208; 1919, **20**, 127, 529; 1920, **21**, 591; *Naturwiss.*, 1919, **7**, 611; *Ber.*, 1919, **52B**, 1812; 1921, **54B**, 69; *Zeitsch. Physik*, 1922, **8**, 202; Gohring sought it but failed to find it, see *Physikal. Zeitsch.*, 1914, **15**, 1642. The actinium series is described in Vol. IV.

[10] See Neuburger, *Sammlung Chemische Vorträge* (Ahrens), 1920–1922, **26**, 315.

[11] Russell, *Nature*, 1923, **111**, 703, from a consideration of the periods of corresponding members of the three disintegration series, concludes that uranium Y is probably derived from an isotope of uranium of atomic weight 240, and that three still unknown members of the series intervene between uranium Y and protoactinium.

[12] Hahn, *Ber.*, 1921, **54B**, 1131; *Naturwiss.*, 1921, **9**, 84, 236; see *Chem. Zentr.*, 1921, i, 1015.

first with uranium X_1, from which it can then be separated by the addition of lanthanum and tantalum solutions. The lanthanum and uranium X_1 together are precipitated by hydrofluoric and sulphuric acids, and subsequently the tantalum remaining in solution is made insoluble by evaporation and ignition, the uranium Z remaining with it.

Uranium Z is isotopic with protoactinium, and has a period of half-change of 6·7 hours.[1,2] It emits a highly complex β-radiation, of which the intensity, however, is only 0·25 per cent. of that of uranium $(X_1 + X_2)$. Its parent must be either uranium X_1 or an unknown isotope of uranium X_1 of similar period. On the supposition that it comes from uranium X_1, Hahn suggests the following scheme :—

$$\text{Uranium I} \xrightarrow{a} \text{Uranium } X_1 \underset{\beta}{\overset{\beta}{\rightleftharpoons}} \begin{array}{c} \text{Uranium Z} \\ \text{Uranium } X_2 \end{array} \underset{\beta}{\overset{\beta}{\rightleftharpoons}} \text{Uranium II} \xrightarrow{a}$$
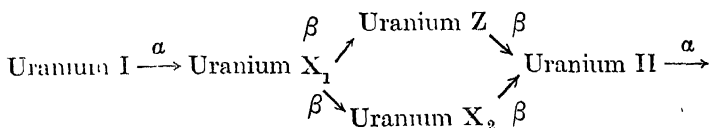
The fraction of uranium forming uranium Z is only about 0·35 per cent.[1]

Hahn also suggests the possibility of a new, independent, but analogous series deriving from an unknown isotope of uranium, uranium III, of probable atomic weight 240,[3] as follows :—

$$\text{Uranium III} \longrightarrow \text{Uranium } Z_1 \longrightarrow \text{Uranium } Z_2 \longrightarrow \text{Uranium IV} \longrightarrow$$
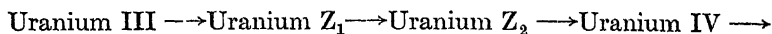
The atomic weight of uranium I might then be regarded as exactly 238.[4] There is not much evidence for either scheme at present, however, but Guy and Russell favour its derivation from uranium X_1.[2]

The possibility of transformation by the emission of isotopic a-particles of mass 3 has been suggested,[5] but there are no experimental grounds for this view.[6]

A substance, uranium V, of period 48 days, giving a soft β-radiation, has been described as separating with uranium X_1 when uranium nitrate is extracted with ether,[7] but this is contradicted by Hahn.[8]

The existence of radio-uranium, the element formerly described by Danne,[9] has never been confirmed.[10]

[1] Hahn, Zeitsch. physikal. Chem., 1923, 103, 461.
[2] Guy and Russell, Trans. Chem Soc., 1924, 123, 2618.
[3] See also Piccard, Arch. Sci. phys. nat. de Genève, 1917, 44, 161 ; Johnstone and Boltwood, Phil. Mag., 1920, [6], 66 ; Joly, Nature, 1922, 109, 480. But see Meyer and Paneth, Sitzungsber. K. Akad. Wiss. Wien, 1912, 121, [2a], 1403.
[4] The atomic weight of uranium is 238·175, Hönigschmid, Zeitsch. Elektrochem., 1914, 20, 452 ; Compt. rend., 1914, 158, 2004 ; Hönigschmid and Horovitz, Monatsh., 1916, 37, 185.
[5] Neuburger, loc. cit. ; Naturwiss., 1921, 9, 235, see Chem. Zentr., 1921, i, 1015 ; see also Smekal, Naturwiss., 1921, 9, 77, 93.
[6] Hahn, ibid., 1921, 9, 236, see Chem. Zentr., 1921, i, 1015 ; see also Meitner, Zeitsch. Physik, 1921, 4, 146 ; Naturwiss., 1921, 9, 423.
[7] Piccard and Stahel, Physikal. Zeitsch., 1922, 23, 1.
[8] Hahn, ibid., 1922, 23, 146.
[9] Danne, Compt. rend., 1909, 148, 337 ; Le Radium, 1909, 6, 42.
[10] See Sirk, Monatsh., 1912, 33, 289 ; Lloyd, J. Physical Chem., 1910, 14, 509.

RADIUM AND GEOLOGY.

The Age of Rocks.—As a result of the α-radiation, radioactive minerals contain occluded helium.[1] If none of this has escaped since the time of formation of the mineral, a comparison of the helium present, with the amount of thorium or uranium in the mineral, should give a means of calculating its age from the formula, age$=\dfrac{\text{He}}{\text{U}}\times 9\cdot 3$ millions of years. Owing to the possibility that helium may have escaped, it will be a minimum age that is thus obtained.[2] The following values have been found from the helium-uranium ratio [3, 4, 5] :—

Geological Period.	Millions of Years.	Geological Period.	Millions of Years
Pleistocene .	0 1–1	Cambrian .	141
Pliocene . .	2·5	Carboniferous .	147
Miocene . .	6 3	Predevonian .	209
Devonian .	54	Archean . .	141–622

Since lead is the ultimate product of uranium and thorium, and possibly also of actinium, another method of determining the age of minerals is indicated. The formula required is $\dfrac{\text{Pb}}{\text{U}}\times 8200$ millions of years. In this case, however, a maximum value is found, since, besides thorium- and uranium-lead, there may also be ordinary lead present. A more precise estimation may be obtained if the atomic weight of the lead be also determined. For a pure uranium mineral it will vary between 206 and 207·2, the atomic weights of uranium-lead and ordinary lead respectively.[5] This has been done for a bröggerite or Norwegian pitchblende. The atomic weight of the lead was 206·12, indicating about 90 per cent. of uranium-lead.   The age calculated was 950 million years.[6]

Holmes calculated the following ages for different types of rock from the lead-uranium ratio [7] :—

Geological Period.	Millions of Years.	Geological Period.	Millions of Years.
Carboniferous . .	340	Precambrian—	
Devonian . .	370	(a) Sweden .	1025–1270
Precarboniferous .	410	(b) U.S. America	1310–1435
Silurian or Ordovician	430	(c) Ceylon . .	1640

[1] Strutt, *Proc. Roy. Soc.*, 1908, 80A, 572 ; 81A, 272 ; 1909, 83A, 96, 298 ; 1910, 84A, 194 ; *Nature*, 1909, 81, 158 ; 1910, 85, 6, 43.
[2] Strutt, *Proc. Roy. Soc.*, 1909, 82A, 166.
[3] Strutt, *ibid.*, 1909, 83A, 298.
[4] Holmes, *The Age of the Earth* (Harper), 1913, p. 156.
[5] See Gleditsch, *Conférence faite devant la Soc. chim. de Fr.*, Strasbourg, May 14, 1920.
[6] Gleditsch, *loc. cit.* ; *Archiv f. Math. og Naturvidenskab.*, *Kristiania*, 1919, No. 36, 1.
[7] Holmes, *loc. cit.* ; *Proc. Roy. Soc.*, 1911, 85A, 248 ; Holmes and Lawson, *Phil. Mag.*, 1914, [6], 28, 833 ; see also Boltwood, *Amer. J. Sci.*, 1907, [4], 23, 77.

All the values obtained from radioactive data are much higher than those found by calculation from sedimentation or denudation.[1]   Joly is inclined to doubt the ages deduced from radioactive data, for it must be remembered that the latter method requires the constancy of the rate of radioactive change over millions of years.[2]

Pleochroic Haloes.—In various minerals, such as mica, cordierite, hornblende, chlorite, tourmaline, etc., minute specks of diameter 0·01–0·02 mm. have been observed.   They are made up of a central nucleus surrounded by concentric coloured spheres.   This nucleus is usually composed of a minute crystal of zircon, although other minerals, for example, apatite, epidote, rutile, or sphene, are possible.   A radioactive origin is ascribed to these pleochroic haloes as they are called.[3]   The coloration of the minerals is supposed to be produced by the action of α-rays from radioactive substances contained in the central nucleus.   The different distances of the rings from the centre are accounted for by the different ranges of the α-rays from the disintegration products of the uranium and thorium present in the nucleus.   The range in air is reduced about two hundred times in mica.[4]

One interesting and curious phenomenon has been noticed in connection with pleochroic haloes.   The older the mineral in which they are found the larger the diameter of the haloes.   For Mourne mica the diameter is 0·0136 mm. ;   for Ballyellen mica, 0·0146 ;   for Rapakivi granite, 0·0152 ;   for Arendal mica, 0·0155 ;   and for Ytterby mica, 0·0160 mm.   This may be explained either by supposing that the rate of decay has diminished, and, therefore, the α-particles now produced are of shorter range than formerly, or that the long range α-particles are derived from an isotope of uranium which has now almost completely disappeared.[5]

By comparing the depth of tint with that of artificially prepared haloes, and by making certain assumptions as to the quantity of radioactive matter in the nucleus, approximate determinations of the age of the minerals may be made.   Results of the same order as those derived from the lead-uranium ratio are obtained.[6]

Bleached or reversed haloes have also been found.   They were at first attributed to the action of heat on the original coloured haloes, but are now thought to be of radioactive origin, the effect being comparable to the reversal of negatives to positives in photography by prolonged exposure.[7]

In some of the uranium haloes of the Arendal mica a minute ring, corresponding to an α-particle of range 1·4 to 1·5 cm. in air, has been observed.   This, according to Joly, may be due to a hitherto unknown element, perhaps no longer existent, which he names, provisionally, hibernium,[8] or it may also be due to a known element of so feeble a

[1] Strutt, *Proc. Roy. Soc.*, 1909, 83A, 97.
[2] Joly, *Phil. Mag.*, 1911, [6], 22, 357 ; *Nature*, 1922, 109, 480 ; Laby, *Le Radium*, 1912, 9, 21.
[3] Joly, *Phil. Mag.*, 1907, [6], 13, 381 ; 1910, 19, 327 ; Joly and Fletcher, *ibid.*, 1910, 19, 630 ; see also section on α-Rays.
[4] See Holmes, *Age of the Earth* (Harper), 1913, p. 109.
[5] Joly, *Phil. Trans.*, 1917, 217A, 51 ; *Nature*, 1922, 109, 480 ; *Proc. Roy. Soc.*, 1923, 102A, 682.
[6] Joly and Rutherford, *Phil. Mag.*, 1913, [6], 25, 644.
[7] Joly, *Proc. Roy. Soc.*, 1923, 102A, 682.
[8] Joly, *Nature*, 1922, 109, 517, 578.

radioactivity that no other known method could detect it.[1]   These haloes may be chance survivals from a period preceding the thermal conditions which generally prevailed during Archæan times, and which must have been responsible for wiping out most of the haloes formed previous to that time.

Larger haloes, showing a range corresponding with 2·25 cm. in air, have also been found, and others of a type similar to the thorium halo, but without the exterior ring, and sometimes containing bleached bands. These Joly calls the X-haloes,[2] distinguishing two varieties, X_1 and X_2.[1]

It is interesting to observe that haloes indicate the existence of far smaller quantities of radioactive matter than can be detected by any other known method.[1]

The Temperature of the Earth.—Another question of interest to geologists is the effect of radioactive change on the temperature of the earth.   Basing calculations of the thermal energy of the earth on the supposition that the average radioactive content of the rocks is the same throughout the whole mass, it was found that enough heat would have been supplied in one thousand million years to raise the temperature of the earth to about 40,000° C.   To explain the existing conditions, the centre of the earth has been assumed to be non-radioactive, the radioactive portion being limited to a crust of about 20 kilometres depth.[3]

THE RADIUM STANDARD.

Radium preparations containing more than 0·01 mgm. of radium may be standardised by comparison of the γ-radiation under specified conditions with that of a standard.   An International Commission met in 1912 to compare standards prepared by Mme. Curie and Hönigschmid. They agreed within the limits of experimental error, and Mme. Curie's was accepted as the International Standard to be kept at the Bureau International at Sèvres, near Paris.[4]   Spectroscopic examination of Hönigschmid's standard showed that it could not contain more than 0·004 per cent. of barium.[5]

In 1914 Rutherford recalculated the various constants for radium on the basis of the International Standard.[6]

[1] Joly, *Trans. Chem. Soc*, 1924, **125**, 897.

[2] Joly, *Proc. Roy. Soc.*, 1923, **102A**, 682.

[3] See Holmes, *The Age of the Earth* (Harper), 1913, p. 131.

[4] Debierne, *Le Radium*, 1912, **9**, 169 ; Rutherford, *Radioactive Substances and Their Radiations* (Cambridge University Press), 1913, p. 657 ; *Nature*, 1912, **89**, 115 ; 1913, **92**, 402.

[5] Haschek and Hönigschmid, *Monatsh.*, 1913, **34**, 351.

[6] Rutherford, *Phil. Mag.*, 1914, [6], **28**, 320.

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as this would render them unnecessarily bulky and expensive ; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xv–xvii.

The addition of the *Table of Dates of Issue of Journals* (pp. xix–xxvi) is hoped, enhance the value of this series. It is believed that it is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr. F. W. Clifford and his staff. To these gentlemen, the Editor and the Author desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin and Co., who have done everything in their power to render the work straightforward and easy.

<div style="text-align: right">J. NEWTON FRIEND.</div>

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